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SPECIAL ISSUE

Optimization and Control of Petroleum Refinery Wastewater Treatment Systems With a Focus on Toxic Contaminants

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FOREWORD

Optimization and Control of Petroleum Refinery Wastewater Treatment Systems With a Focus on Toxic Contaminants

In both Canada and the United States, regulatory requirements to control the discharge of toxic contaminants to the environment have placed stringent demands on existing wastewater treatment facilities. The petroleum industry, along with all other industrial sectors, will need to produce a treated effluent quality far superior to that for which their facilities were originally designed. Trace contaminant control and toxicity reduction, rather than removal of conventional contaminants, has become the goal. Attaining this goal will require an understanding of petroleum refinery wastewater treatment processes beyond the present level so that optimum performance can be achieved.

On March 6 and 7, 1989, a workshop was held at the Canada Centre for Inland Waters in Burlington, Ontario to discuss innovative and economic methods of improving the performance of petroleum refinery wastewater treatment systems through process optimization.

The workshop, which was cosponsored by the Petroleum Association for Conservation of the Canadian Environment (PACE), the American Petroleum Institute (API) and the Canadian Association on Water Pollution Research and Control (CAWPRC), featured introductory sessions by technical experts in the areas of petroleum refinery wastewater treatment plant design and operation, treatment process optimization and toxics removal. A series of workshop sessions followed to promote discussion and technical interchange. The program concluded with a summation of the discussions in the workshops, keying on proven solutions and identifying areas where further knowledge was needed.

This special issue of the *Water Pollution Research Journal of Canada* represents a compendium of the information presented at the workshop. The contents of the special issue reflect the opinions of the authors and should not be considered to represent the views of the sponsoring agencies.

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Developments in Legislation Related to Treatment of Petroleum Refinery Effluents: A Canadian Overview

David L. Putnam[1]

Abstract

Public concern over toxic contaminants in drinking water and the environment in general has put increasing pressure on governments to develop and enforce stringent environmental regulations. An overview of developments in Canadian federal and provincial legislation related to the regulation of petroleum refinery effluent quality is provided. Current knowledge of Canadian petroleum refinery effluent quality and level of treatment is summarized.

Introduction

The driving force behind water quality improvement and the trend towards more stringent environmental regulations in general is increasing public concern over the quality of the environment. Public knowledge and concern about trace contaminants has been enhanced by advances in analytical techniques that allow detection of chemicals at very low concentrations. A Fall 1987 Decima Poll (Powicki 1989) identified health risks related to toxic chemicals in drinking water as the major environmental concern. This concern is reflected in the recent enactment of statutes such as the Canadian Environmental Protection Act and regulatory programs such as the Ontario Municipal Industrial Strategy for Abatement (MISA) program.

This paper provides an overview of the legal framework in which federal and provincial regulators control Canadian water quality and a summary of the efforts by the Canadian petroleum industry to characterize its effluent quality and level of treatment.

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The Legal Framework For Regulation of Canadian Water Quality

Federal-Provincial Jurisdiction

In Canada the responsibility for water pollution control is shared between the federal and provincial governments. In the past, the division of jurisdictional authority over water quality has been a source of tension between the federal and provincial regulators. Questions over jurisdiction arose from ambiguities in the assignment of federal and provincial authority by the Constitution Act. To provide coordination of federal and provincial activities, seven of the provinces have signed Accords with the federal government outlining a general framework for administrative cooperation (Pearse *et al.* 1985).

The federal government's responsibilities involve establishing national ambient water quality objectives and developing standards and guidelines for effluents on a consultative basis with industry. Regulations have been adopted for six industrial sectors: petroleum refining, pulp and paper, chlor-alkai, meat and poultry products, potato processing and metal mining. For these sectors, uniform baseline effluent standards are applied as minimum requirements throughout Canada. Petroleum refineries are controlled at the federal level under the Fisheries Act, an old statute that actually predates Confederation. The Fisheries Act prohibits the disturbance and pollution of fish habitats and controls refinery discharges through a set of regulations and guidelines published in the Canada Gazette in 1973.

Refinery discharges are controlled at the provincial level on an individual basis by issuing discharge permits. Discharge permits usually contain site specific regulations that limit the concentration of suspended solids, toxic substances and organics that increase biological oxygen demand. Factors considered when setting the effluent limits include receiving water use, upstream water quality, plant location and age. The provinces have assumed the responsibility to establish and enforce effluent standards at least as stringent as the national baseline standards at all new facilities and at all existing facilities as soon as practicable. The provincial jurisdiction also includes ensuring that discharge permit holders comply with the terms of the permit.

The provinces of British Columbia, Alberta, Ontario and Quebec have established water quality criteria based on the protection of aquatic life and water recreation in order to maintain a desired quality of water (Pearse *et al.* 1985). In other provinces, control of effluent discharges is based on the federal regulations or guidelines.

Canada has no legislated national drinking water standards. Quebec is the only province that has incorporated such standards into provincial legislation. The other provinces have adopted guidelines prepared by a joint federal/provincial committee.

The Canada Water Act (1970)

In 1970, the federal government enacted the Canada Water Act to address generally the single issue of freshwater management. The Canada Water Act has a much broader scope than the legislation it replaced, the Conservation Assistance Act (1953) which was enacted to provide government assistance for building water storage facilities. Because the federal government has limited constitutional authority in water management, the Canada Water Act emphasizes federal-provincial cooperation and authorizes the federal government to join the provinces in a wide range of water management activities. These activities include planning and implementing projects.

The Canada Water Act has been criticized for being ineffective for several reasons. First, it severely limits the federal government's ability to respond to water pollution problems. For other than federal waters, the federal government can act only when water quality has been degraded to a point of "urgent national concern". Second, a province is subject to a greater threat of unilateral federal intervention if it enters into a water quality agreement with the federal government.

Other statutes which play a role in maintaining Canadian water quality but are not specifically related to the control of trace contaminants include the Canada Shipping Act (1970), the Northern Inland Waters Act (1970) and the Ocean Dumping Act (1974).

The Environmental Contaminants Act (1975)

Prior to 1988, the Environmental Contaminants Act was the major instrument for federal control of toxic pollutants. In June 1988, this statute was incorporated into the Canadian Environmental Protection Act. The purpose of the Environmental Contaminants Act is to prevent dangerous contaminants from entering the environment. This Act gives the federal government power to prevent certain serious types of water pollution. It authorizes the Minister of Health and Welfare and the Minister of the Environment, to jointly prepare a list of substances considered to pose a significant threat to human health or the environment. After a substance has been listed, its release to the environment is strictly regulated. Only five substances

have been listed to date: polychlorinated biphenyls (PCB's), polybrominated biphenyls (PBB's), polychlorinated terphenyls (PCT's), mirex and chlorofluorocarbons.

The Canadian Environmental Protection Act (1988)

In June 1988, Canada promulgated the Canadian Environmental Protection Act (CEPA). CEPA takes an ecosystem approach to environmental protection by treating the environment as a closed system. CEPA incorporates several existing statutes covering all aspects of the environment, including sections of the Canada Water Act, the Environmental Contaminants Act, the Ocean Dumping Act and the Clean Air Act.

CEPA serves to prevent threats to human health and the environment by regulating toxic substances from "cradle-to-grave", i.e. from production to final disposal. Any substance potentially threatening to human health or the environment may be considered "toxic". Candidates for regulation by the Act include organic and inorganic chemicals, emissions, effluents, wastes, and genetically engineered organisms.

Under CEPA, Environment Canada is responsible for assessing environmental impacts and Health and Welfare Canada for determining the human health effects. Substances meeting certain toxicity criteria will be placed on the List of Toxic Substances. Presently the List of Toxic Substances consists of four substances from the Clean Air Act (asbestos, mercury, lead and vinyl chloride) and five substances from the Environmental Contaminants Act (PCB's, PPB's, mirex, CFC's and polychlorinated terphenyls).

Regulations and codes of practice will be developed to control the contaminants on the Toxic Substances List. Regulations which are enforceable by law will set numerical limits on the quantities of those substances manufactured, imported and released to the environment in industrial effluents. Codes of practice, rather than being enforceable by law, are voluntary and serve to complement regulations. Codes of practice deal with the best available techniques for manufacturing, handling, and disposal of a toxic substance. CEPA provides Environment Canada with the authority to ban a substance based on the results of the health and environmental risk assessments.

Included under CEPA is an enforcement and compliance program requiring regular inspection of areas where a toxic substance is regulated. To ensure compliance by industry, monitoring of the water, soil, air and marine environment for a regulated substance is mandatory.

To reduce potential disputes over federal and provincial powers, CEPA was redrafted several times and equivalency provisions inserted. Equivalency provisions allow the federal government to waive certain CEPA regulations in a province or territory where equivalent or more stringent provincial regulations exist. The province or territory is responsible for enforcing its regulations, while the federal government monitors provincial enforcement efforts to ensure compliance to national standards.

The large overlap between federal and provincial jurisdiction will likely continue to be a source of contention during the implementation of CEPA, as it represents an extension of federal jurisdiction over environmental matters.

The Ontario Municipal-Industrial Strategy for Abatement (MISA)

The MISA program, first announced in 1986, is an ambitious program which will have a large impact on the development of pollution control technology and will serve as a model for regulation of effluent quality by the other provinces of Canada. Regulations governing the effluent quality of nine industrial sectors and the municipal sewage treatment plants will be promulgated under the Ontario Environmental Protection Act (Ontario Ministry of the Environment 1986).

The ultimate goal of the program is the reduction of all industrial and municipal waste loadings and the virtual elimination of all persistent toxic contaminant discharges into Ontario waterways. The strategy consists of components for monitoring and compliance regulations.

The monitoring regulation requires characterization, routine monitoring, flow measurement, sampling and analytical protocols, and toxicity testing. It requires dischargers to characterize their effluents in terms of the traditional conventional pollutants as well as a select group of pollutants from the Effluent Monitoring Priority Pollutant List (EMPPL). The characterization process must be performed once every three years, or after a significant change to the process has occurred. Routine monitoring involves testing for subsets of the EMPPL on daily, weekly, and quarterly frequencies. Compliance regulations will be developed or revised based on data generated during the monitoring process, technology and economics, historical effluent quality and receiving water quality.

Central to the development of compliance regulations is establishing a definition for the best available technology economically achievable (BATEA). The application of BATEA to effluent treat-

ment is a on-going process that is expected to require periodic review. New and lower effluent limits may be implemented as a result of the development of improved treatment technologies, degradation of receiving water or the addition of new chemicals to the EMPP list. Once a chemical is added to the list, dischargers will be required to monitor their effluent for its presence and provide treatment if detected. BATEA is not restricted to end-of-pipe treatment and may include other measures such as process modifications, substitution of less toxic chemicals, recycling and in-plant treatment. This process should force the development of new control technologies and optimization of existing treatment systems.

The first monitoring regulation was promulgated in June 1988 for the petroleum industry (Ontario Ministry of Environment 1988). Monitoring regulations were issued for the organic chemical sector in March 1987. Regulations for other industrial sectors including iron and steel, pulp and paper, mining, metal casting, inorganic chemicals, and municipal sewage treatment plants will follow. Compliance regulations for the petroleum industry are expected by 1991.

Control of Trace Contaminants in Petroleum Refinery Effluents

Since the early 1970's, concern over trace contaminants in the environment has been growing due to increasing public awareness of the large number of toxic chemicals present in natural waters and drinking water supplies.

On November 1, 1973 the Canadian Petroleum Effluent Regulations and Guidelines (Environment Canada 1979) were issued pursuant to the Federal Fisheries Act. The Regulations, enforceable by law, apply to refineries that came on stream after the regulations were issued. For those facilities in operation before November 1, 1973, the guidelines apply as codes of practice without the force of the law.

The regulations and guidelines limit the deposit of "conventional" pollutants including oil and grease, phenols, sulphide, ammonia nitrogen, total suspended solids and pH levels. In addition, the regulations and guidelines specify methods of monitoring and reporting frequency.

The purpose of the regulations and guidelines is to guarantee that all Canadian refineries apply the "Best Practicable Technology (BPT)" to their liquid effluents.

BPT is defined under the regulations and guidelines as:

1. Sour water stripping for ammonia and sulphur removal;
2. Primary separation (API separator) followed by;
3. Intermediate treatment (e.g. air flotation) followed by;
4. Secondary treatment (e.g. biodegradation);
5. Final effluent clarification as required;
6. Segregation and treatment of stormwater if required.

In 1975, media coverage of health risk studies related to chemical spills the U.S. generated sufficient public concern that several environmental groups collaborated in bringing suit against the U.S. EPA. The groups charged that insufficient monitoring and enforcement was compromising the public's health. The result was the signing of the 1976 Consent Decree, obligating the U.S. federal government to enforce "Best Available Treatment" technology to control the discharge of toxic contaminants in twenty-one industrial sectors (Tischler and Kocurek 1989). The Decree included a list of one hundred and twenty-nine contaminants identified as substances requiring regulatory action. The list came to be known as the "EPA Priority Pollutants List".

In Canada, the same concern over toxic contaminants led to the promulgation of the Environmental Contaminants Act (1975). The "Priority and Candidate Chemicals List" included in this Act consisted of twenty-six contaminants or groups of compounds. The majority of these contaminants were chlorinated organics and trace metals not normally found in refinery effluents. For this reason, the Canadian refineries were not forced by regulations to monitor for the full range of contaminants.

Growing public concern over toxic contaminants and a trend towards more stringent environmental regulations prompted PACE, in conjunction with Environment Canada, to commission a series of scientific investigations into the presence of trace contaminants in refinery effluents (PACE 1981; 1985a; 1985b; 1985c; 1987). Monitoring for these studies was based on the U.S. EPA Priority Pollutants List. These studies showed that most of the metals on the U.S. EPA list were detected in wastewaters within the treatment units and detectable at lower concentrations, less frequently, in the final effluent. Eighty percent of the U.S. EPA organic priority pollutants were not routinely detected in refinery wastewaters. Most of the organic compounds that were detected were common constituents of crude oil.

The priority contaminants routinely detected in refinery effluents include benzene, toluene, ethylbenzene, naphthalenes, phenols, zinc and chromium. Polyaromatic hydrocarbons and phthalic acid

esters were infrequently detected at very low concentrations. Derivatives of the above compounds were also detected occasionally at low levels. The level of trace contaminants found in refinery effluents generally comply with water criteria issued by international, Canadian and U.S. regulatory agencies.

One of the objectives of the PACE/Environment Canada studies was to evaluate the fate and transformation of trace organics in refinery wastewater treatment systems. These studies demonstrated that at the current level of treatment technology used at Canadian refineries, a properly operated wastewater treatment system is very efficient at removing organic priority pollutants.

Oil and grease removal by the API separator and air flotation units followed by biological oxidation are the treatment system processes most effective at reducing trace organics. Adsorption to sludges and volatilization to the atmosphere act to remove pollutants to a much lesser extent. However, priority pollutants have occasionally been detected in oily sludges. The effectiveness of refinery wastewater treatment for trace organics and metals is indicated by a system's treatment efficiency for conventional parameters such as phenols, oil and grease, suspended solids, and total organic carbon.

The results of the studies initiated by PACE and Environment Canada serve to characterize the trace contaminant content of refinery effluents and to demonstrate the effectiveness of Canadian refinery treatment systems for removal of trace contaminants. Because most of the trace contaminants being monitored were often not detected, statistical correlations between treatment system operating parameters and levels of specific contaminants could not be established.

Summary

In the U.S., regulation of refinery effluent quality under the Clean Water Act involves limits for toxicity and trace contaminants and the mandatory use of BATEA for effluent treatment. This approach is central to the Ontario Ministry of Environment's MISA program and will likely set the trend for the other provinces in Canada. The on-going review of effluent quality and BATEA under these programs should provide the impetus for improved system design, process control and optimization of effluent treatment system performance.

Key words: Canadian Environmental Protection Act (CEPA), Municipal-Industrial Strategy for Abatement (MISA), Best Available Technology Economically Achievable (BATEA), Best Practical Technology (BPT), EPA Priority Pollutants List, Petroleum Association for Conservation of the Canadian Environment (PACE)

References

Environment Canada (1979), "Petroleum Refinery Effluent Regulations and Guidelines". Water Pollution Control Directorate. Report EPS 1-WP-74-1.

Ontario Ministry of the Environment (1986), "Municipal-Industrial Strategy for Abatement (MISA)". A Policy and Program Statement of the Government of Ontario on Controlling Municipal and Industrial Discharges into Surface Waters. Toronto. 1986.

Ontario Ministry of the Environment (1988), "Effluent Monitoring Regulations for the Petroleum Refining Sector". Ontario Reg. 358. July 1988.

Pearse, P.H., F. Bertrand and J.W. MacLaren (1985), "Currents of Change". Final Report — Inquiry on Water Quality. September 1985. Ottawa, Ontario. ISBN 0-662-14189-X.

Powicki, C.R. (1989), "Standing on Guard for Thee: The Canadian Environmental Protection Act". *Journal WPCF* **61**, 585–593.

PACE (1981), "Survey of Trace Substances in Canadian Petroleum Industry Effluents". The Petroleum Association for Conservation of the Canadian Environment. Report 81-4. Ottawa, Ontario.

PACE (1985a), "Evaluation of the Variability of Trace Organic Substance in Petroleum Refinery Effluents". The Petroleum Association for Conservation of the Canadian Environment. Report 85-6. Ottawa, Ontario.

PACE (1985b), "Fate and Transformation of Selected Trace Organic Substances in Refinery Wastewater Treatment". The Petroleum Association for Conservation of the Canadian Environment. Report 85-7. Ottawa, Ontario.

PACE (1985c), "A Survey of Trace Substances in Canadian Oil Refinery Wastewaters and Sludges — A Summary Report". The Petroleum Association for the Conservation of the Canadian Environment. Report 85-8. Ottawa, Ontario.

PACE (1987), "Sampling and Analysis of Refining Effluents to Assess Variations in Trace Contaminant Concentration". The Petroleum Association for Conservation of the Canadian Environment. Report 87-2. Ottawa, Ontario.

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Developments in Legislation Related to Treatment of Petroleum Refinery Effluents: A U.S. Overview

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Abstract

Regulatory requirements in the United States controlling wastewater pollutants and toxicity resulting from point sources, such as refineries, emanated from passage of the Federal Water Pollution Control Act in 1972 and its subsequent amendments, collectively referred to as the Clean Water Act. The Clean Water Act empowers in the federal U.S. Environmental Protection Agency and states to issue effluents limitation guidelines and water quality standards to point sources that discharge pollutants directly to surface waters. These guidelines and standards are contained in permits issued under the National Pollutant Discharge Elimination System. The current regulatory emphasis on toxics probably will lead to more stringent pretreatment standards and reduced refinery wastewater flow.

Introduction

In both Canada and the United States, regulatory requirements to control wastewater toxicity resulting from refinery effluents are placing stringent demands on refineries to improve their wastewater treatment process. The following is an overview of the evolution of clean water legislation as it relates to U.S. refineries.

Clean Water Legislation

The Federal Water pollution Control Act of 1972 (FWPCA) established the basic framework for federal water pollution control

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regulation. Its objective was "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters." The Act has been amended several times — most significantly by the Clean Water Act (CWA) in 1977 and by the Water Quality Act (WQA) in 1987. Since 1977, the Act and its amendments have been commonly known as the Clean Water Act.

The CWA protects the nation's waters from pollution from point sources — such as petroleum refineries and other industrial plants, municipal sewage treatment plants (Publicly Owned Treatment Works or POTWs), and agricultural feedlots — and non-point sources — such as agriculture, mining and urban runoff.

The CWA is implemented by the Environmental Protection Agency (EPA) and authorized states. EPA issues effluent limitation guidelines. The individual states set water quality standards to protect waterways for such designated uses as fishing and swimming. The states review these standards at least once every three years.

Effluent limitation guidelines and water quality standards are applied to point sources that discharge pollutants directly to surface waters through the issue of individual discharge permits under the National Pollutant Discharge Elimination System (NPDES). Under this system, permitees must limit the amount of pollutants discharged and submit periodic monitoring reports.

To renew a permit, a discharger must submit an application six months before the old permit expires to allow time to develop new permit conditions and to allow EPA to comply with procedural requirements, such as a public notice and a public hearing. If the permitee makes timely application for a renewal, the terms of the existing permit continue in effect until the new permit is issued. Many U.S. refineries, whose permits will soon expire, are now preparing their renewal applications.

Point sources that discharge pollutants indirectly into POTWs through the sewage collection system are also regulated by pretreatment standards to restrict the discharge of pollutants that would interfere with or pass through the municipal treatment works.

The Federal Water Pollution Control Act of 1972

The major focus of the FWPCA was regulation of end-of-pipe discharges from point sources of conventional pollutants such as biochemical oxygen demand (BOD), suspended solids, fecal coliform, and pH. (EPA later added grease and oil.)

The Act directed EPA to issue effluent guidelines, requiring that existing point sources meet effluent limitations based on the application of "best practicable control technologies" (BPT) and "best

available control technologies" (BAT). These limitations were to be based on what was technologically and economically achievable, not on the quality of receiving waters. BPT limitations were to be based on the "average of the best existing performance by well-operated plants within each industrial category." In establishing BPT, EPA was to consider the total cost of the control in relation to the effluent reduction benefits to be achieved, as well as such other factors as engineering and technical aspects of the processes involved. In establishing BAT, a more stringent control, EPA was to consider cost but not benefits.

The Act also directed EPA to issue New Source Performance Standards (NSPS), applicable to new sources and significant modifications of existing sources, for each industrial category. EPA promulgated NSPS for the petroleum refining point source category on May 9, 1974. In setting the NSPS, EPA was to consider changes in processes and operating methods. EPA was to consider the cost of achieving the standards but was not required to compare them with effluent reduction or water quality benefits.

The Act further required that more stringent controls be imposed on any plant when necessary to ensure that state water quality standards were met. These additional measures were to be written into NPDES permits.

The Clean Water Act of 1977

The CWA amendments comprised several major changes of importance to refineries. Apart from the extension of deadlines, the most important changes were:

(1) to create a new standard for conventional pollutants,
(2) to redirect BAT limitations to emphasize toxic pollutant controls,
(3) to establish a new category of "non-conventional" pollutants and to subject them to BAT,
(4) to authorize EPA to issue regulations on "best management practices" (BMPs), and
(5) to modify pretreatment requirements

Conventional Pollutants: Congress established a new standard for conventional pollutants, called the Best Conventional Pollutant Control Technology (BCT) standard. In determining what constitutes BCT, EPA was to (1) compare the costs and effluent reduction benefits of controls and (2) compare the costs and effluent reduction benefits of controls imposed by industrial plants with those imposed by municipal treatment plants.

Toxic Pollutants: BAT standards for industry were to cover 65 priority pollutants and pollutant classes on a specific list drawn up by EPA. Listed toxics include arsenic, asbestos, cyanides and lead.

Non-Conventional Pollutants: BAT standards were to be set for non-conventional pollutants — those not specifically identified as either conventional or toxic and including such pollutants as aluminum, iron, chlorine, ammonia, fluoride, phosphate, nitrate, chemical oxygen demand and color.

BMPs: BMP regulations were to be issued to control runoff, spillage or leaks of toxic and hazardous materials from industrial sites.

Pretreatment: Direct dischargers of toxic pollutants were to receive credit for any removal of these pollutants by POTWs.

The Water Quality Act of 1987

The WQA amended the CWA in several ways important to refineries. EPA and the states have already implemented some of these changes and plan to implement others by 1990. At a March 1989 conference for state officials, EPA discussed still other changes that it hopes will be implemented between fiscal years 1991 and 1996.

Amendments Now Being Implemented

Major WQA amendments now being implemented are those regarding the listing of waters that have not achieved state water quality standards, adoption of numeric criteria for toxic pollutants by the states, and antidegradation.

Listing of Waters: The WQA added section 304(1) to the CWA to push the states to clean up waters that had not yet achieved water quality standards. The new section requires states to submit lists of waters that had not achieved state water quality standards because of discharge of listed toxic pollutants. For the latter, the states were required to develop permit limitations, called Individual Control Strategies (ICSs), to be applied to sources identified as discharging toxic pollutants into the listed water body. The states' lists and ICSs, to be approved by EPA, must require the rapid achievement of water quality standards.

Numeric Criteria for Toxics: The WQA required that the states adopt numeric criteria for toxics. Numeric criteria are a number or a set of numbers, such as "2.0 mg/l ammonia," as opposed to "narrative" standards, which are descriptive statements, such as "no discharge of toxics in toxics amounts."

Antidegradation: The WQA required that states develop procedures to prevent the degradation of waters whose quality exceeds state water quality standards. To protect these waters, the states must ensure that any economic growth that will impair water quality is necessary and that all alternatives to degradation have been exhausted. No degradation is permitted in waters the states have designated for special protection because of their ecological, recreational or ecological significance.

Amendments to be Implemented Before 1996

The WOA made several other changes, which EPA plans to implement by 1996. In a November 1988 draft framework for the water quality program, EPA outlined its objectives for the fiscal year 1991–1993 triennium. They are to:

- Establish a permanent link between the requirement that states list waters impaired by conventional and toxic pollutants and the requirement that the states adopt numeric criteria in their water quality standards.
- Establish water quality standards for marine, wetland and estuarine systems. Although wetlands are some of the most productive ecosystems in the world, few states have regulatory procedures that protect wetlands.
- Adopt sediment criteria for toxics. Sediment criteria are chemical-specific numeric criteria that define the concentration of toxic contaminants in sediments that, if exceeded, will adversely affect aquatic life, human health and the attainment of related beneficial uses.
- Adopt biological criteria (biocriteria). Biocriteria can be narrative (based on a general statement on biotic integrity, such as it "the resident biological community shall be as it naturally occurs") or numeric (based on one measurement, such as the biomass of fish, or a combination of measurements such as the biomass of fish, or a combination of measurements such as fish diversity, abundance, and habitat quality).
- Integrate Standards and Non-Point Source Control programs. The states are required to identify waters that cannot attain

or maintain water quality standards unless non-point sources of pollution are controlled. States are also required to identify categories of non-point sources that significantly pollute waters.

In the same draft framework, EPA outlined its objectives for the fiscal years 1994–1996. In this time frame, the states are to adopt criteria to protect wildlife and marine/estuarine ecosystems.

Impact of Water Quality Legislation on U.S. Refineries

The current regulatory emphasis on toxics, through permit limits on direct dischargers and pretreatment standards applicable to indirect dischargers, has confronted U.S. refineries with two major issues: the permitting approach based on water quality and refinery effluent guidelines.

Water Quality Approach to Permitting

All of the 56 states and territories have submitted their lists of state waters wherein water quality standards are not being attained. The number of waters on the long lists totalled 17,365 (about 10 percent of the nation's waterways). The most common pollutants on the lists included dissolved oxygen, biochemical oxygen demand (BOD), suspended solids, bacteria, nutrients, organics, pesticides and metals.

The states listed 495 waterways as impaired primarily by point source dischargers and EPA added 100 waterways, making a total of 595. The states indicated that 769 point source discharges were primarily responsible for impairing water quality and EPA added 110 point sources, making a total of 879 (627 industrial facilities, 240 cities, and 12 federal facilities). See Table 1 for a list of the industrial facilities classified by type and number.

For dischargers identified as responsible for a waterway's failure to meet state water quality standards because of discharges of listed toxic pollutants, the states have developed or are developing ICSs. ICSs require the dischargers to identify waste streams contributing to the toxicity and may require them to develop in-plant source controls or upgrade treatment facilities.

Refinery Effluent Guidelines

As a result of the water quality standards and the scheduled revision of the NSPS guidelines, EPA will initiate in 1990 a condensed five-year review program in the hopes of promulgating a final rule by 1994. For refineries, the American Petroleum Institute

Classification		Number
1.	Metal finishing	135
2.	Pulp and paper	94
3.	Natural gas	55
4.	Petroleum refining	21
5.	Organic chemicals	22
6.	Iron and steel	17
7.	Textile mills	16
8.	Ore mining	12
9.	Inorganic chemicals	13
10.	Superfund sites	7
11.	Steam/electric	11
12.	Rubber	7
13.	Plastics and synthetics	5
14.	Leather tanning	5
15.	Food processing	3
16.	Coal	2
17.	Pharmaceuticals	1
18.	Other	102
19.	Unknown	99
	TOTAL	627

Table 1. Number of industrial facilities by type found to be primarily responsible for impairing water quality.

(API) expects EPA to examine wastewater flow reduction (resulting in stricter limits via permits), in-plant source controls for toxics, and end-of-pipe limits on additional pollutants, toxicity limits (bioassay requirements) and implementation of best management practices.

The current regulatory emphasis on toxics and the concern over toxic pollutant discharges to POTWs will probably lead EPA to promulgate regulations requiring direct and indirect dischargers to meet more stringent pretreatment standards. API may respond to this change by sponsoring research to monitor EPA's efforts to refineries, performing statistical analysis of its and EPA's samples, and developing a date base.

Research on the technical feasibility and costs associated with the various options for reducing refinery wastewater flow and improving treatment system efficiencies has also been identified. The development of a date base on the relationship between wastewater

flow, treatment system efficiency and effluent concentrations is also being considered.

References

92nd U.S. Congress (1972), "Federal Water Pollution Control Act of 1972". 33 U.S.C. Section 1251 *et seq.*, Public Law 92-500, October 18, 1972.

95th U.S. Congress (1977), "Clean Water Act of 1977". Public Law 95-217, December 27, 1977.

100th U.S. Congress (1987), "Water Quality Act of 1987". Public Law 100-4, February 4, 1987.

U.S. Environmental Protection Agency, Office of Water (1989), "Water Quality Standards for the Twenty-First Century Conference".

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Current Practice for Treatment of Petroleum Refinery Wastewater and Toxics Removal

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Abstract

Current practice and experience in the treatment of petroleum refinery wastewater is reviewed briefly, with emphasis on the fate of toxic contaminants. The sources and composition of the wastewater are described in terms of the parameters adopted for evaluating the performance of individual treatment units. The parameters include oil and grease content and sulphide concentration for evaluating the primary treatment units: sour water stripping, API separation and dissolved air flotation (DAF). COD, BOD, suspended solids and "listed" trace contaminant concentrations are considered in the description of biological activated sludge secondary treatment. Current treatment technology achieves a significant reduction in toxic contaminants and other pollutants generated in the petroleum refining process, with the principle reduction occurring in the activated sludge system. The removal mechanisms considered in activated sludge are biological degradation, nitrification, stripping of VOC's, biosorption, bioaccumulation of heavy metals and heavy metal precipitation. A number of potential problems associated with activated sludge treatment are identified; amongst others, high effluent COD's, presence of toxic contaminants (at low concentrations) in the treated effluent, inhibition, poor sludge settleability, and waste sludge disposal.

Key words: petroleum refinery wastewater, trace organic contaminants, heavy metals, API separation, DAF, activated sludge, biosorption, stripping, bioaccumulation, inhibition, sludge settleability.

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Introduction

Petroleum refining involves separating and/or transforming the components of the crude oil feedstock into a range of products: amongst others, gasoline, fuel oils, lubricating oils, asphalts and petrochemical industry feedstocks. The refining process consumes large amounts of water, and generates large wastewater flows containing a variety of contaminants. In areas where refining, with its ancillary industries, is practised widely the associated wastewater flow constitutes a major component of the total waste flow to be treated. For example, in the Sanitation District of Los Angeles County the contribution of approximately 23 MGD from refining and related industries constitutes 35 percent of the industrial wastewater generated and 6 percent of the total (municipal plus industrial) for the District (Rhee *et al.* 1987).

The large wastewater flows and the fact that certain "priority pollutants" such as trace organics and heavy metals have been identified in the waste from petroleum refineries has resulted in this industrial sector receiving considerable attention from regulators. Concomitantly, there has been increased interest in the development of technologies for the effective treatment of the waste to remove hazardous contaminants and thereby protect the quality of receiving waters. This paper attempts to provide an overview of current treatment practice. The various treatment steps most commonly encountered are described, with the principal focus being the biological treatment stage and the fate of toxic contaminants.

Sources of Wastes from Petroleum Refining

Crude oil processed in the petroleum refining industry is a complex mixture of chemical compounds. The chief constituent is a range of hydrocarbon compounds comprised of molecules containing approximately four to twenty carbon atoms. The carbon atoms may be linked together in a straight chain, a branched chain or a ring structure. The most predominant hydrocarbons in crude oil are "paraffins" (straight chain saturated hydrocarbons) in which each carbon atom is linked with the maximum possible number of hydrogen atoms; these have the generic chemical formula C_nH_{2n+2}. Hydrocarbons with straight or branched chains, but containing fewer than the maximum possible number of hydrogen atoms, are termed "unsaturated" or "olefins"; these have the generic chemical formula C_nH_{2n}. Hydrocarbons incorporating a ring structure are classified

as "naphthenes"; these include aromatic compounds such as benzene and toluene. In addition to the hydrocarbons, crude oils contain sulphur and nitrogen (each approximately 0.5 to 3% by mass), certain heavy metals, and inorganic salts such as sodium chloride.

Almost every refining operation from primary distillation to thermal cracking to cooling water blowdown generates a wastewater flow. There is also wastewater generation from sources not directly implicated in the refining process; for example, draw off of water from storage tanks, ship ballast water, surface runoff, to name a few. Figure 1, modified from Rhee *et al.* (1987), attempts to illustrate the complexity of the wastewater flow network at a typical refinery. A major component of the water inventory at a refinery (reported as 80 to 90 percent) is cooling water used as a heat transfer medium in the thermal separation processes. At more modern refineries cooling water is recirculated to reduce the overall water consumption. The quantity (and composition) of wastewater will differ significantly between refineries because of differences in: (1) refinery process configuration and operating conditions; (2) product lines; and (3) the composition of the crude oil feedstock.

Composition of Wastes from Petroleum Refining

Large variations in the composition of different wastewater streams within a refinery are encountered. For example, quench waters from asphalt oxidation can be expected to contain significant concentrations of phenolics, while desalter waste will contain primarily inorganic salts. There will also be large differences in parameters such as pH and temperature between streams. Therefore significant potential exists for separate treatment of individual streams. This approach is practised to some degree as reflected in Figure 1. However, the practice is not widely applied, and the tendency has been to combine most wastewater flows in a single stream prior to treatment.

The practice of combined treatment has perhaps arisen from the approach to treatment adopted historically. Traditionally on-site treatment was limited to what is now regarded as the primary stage of treatment; namely, oil and grease removal. This generally involved API separators and dissolved air flotation units for removal of free, dispersed and emulsified oils; dissolved matter was usually directed in the effluent stream sent to a municipal treatment plant. However, as the requirements for on-site treatment become more stringent, the optimal treatment scheme may involve separate treatment of a number of the individual streams. For example, one of the problems in

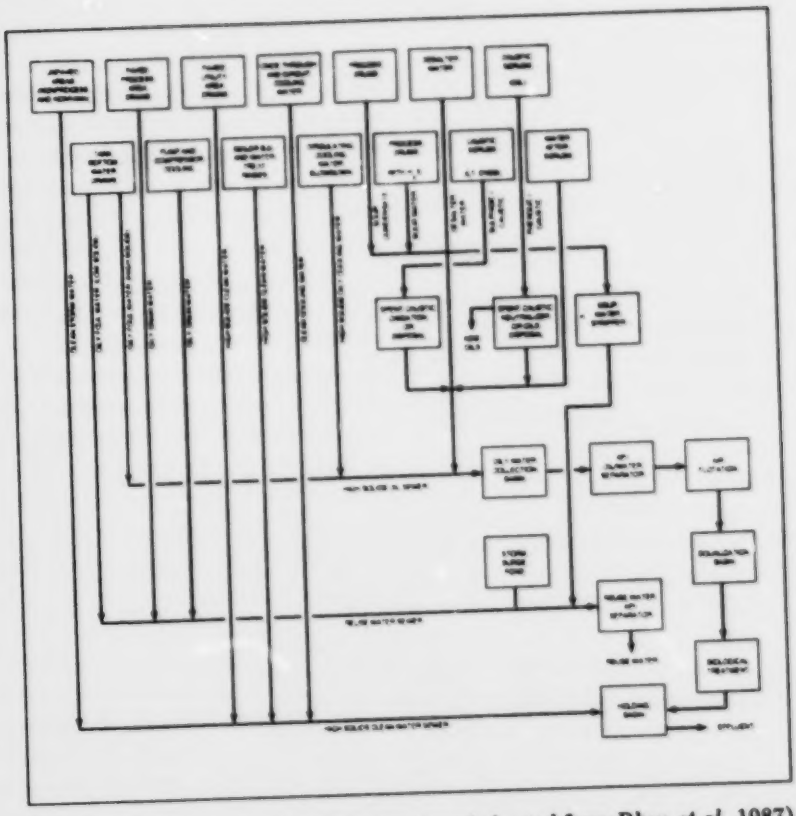

Figure 1. Sources of refinery wastewaters (adapted from Rhee *et al.* 1987).

biological treatment is inhibition caused by phenolic compounds. It may be optimal to gather those streams with high phenolic contents for separate treatment.

The manner of reporting the composition of refinery wastewaters has evolved over the years. Undoubtedly the change has been driven by the increased emphasis on treatment and the increased sophistication of treatment process configurations. As discussed above, initially on-site treatment was largely restricted to primary removal of oil and grease by gravity separation. For this reason refinery waste composition was classified in terms of the oil and grease content, and the size of oil droplets in the oil-water mixture. Figure 2 shows the approximate classification of the oil content based on droplet size. Oil with droplet diameters larger than 150 microns is generally classified as free oil (API 1969); this material is largely removed by API separators. Dispersed oil contains droplets in the approximate size range 20

to 150 microns; the major portion of this material (sizes greater than approximately 40 microns) can be removed by dissolved air flotation (Rhee *et al.* 1987). The droplet size fraction smaller than 20 microns is classified as emulsified oil (Manning and Snider 1983). With decreasing droplet size, a point is reached (approximately 5 microns) where the oil is regarded as soluble. As noted, oil droplets in the oil-water mixture with diameters larger than approximately 40 microns are removed with reasonable efficiency in primary treatment. For increased overall removal efficiency and removal of contaminants in the soluble fraction, the waste must undergo further treatment.

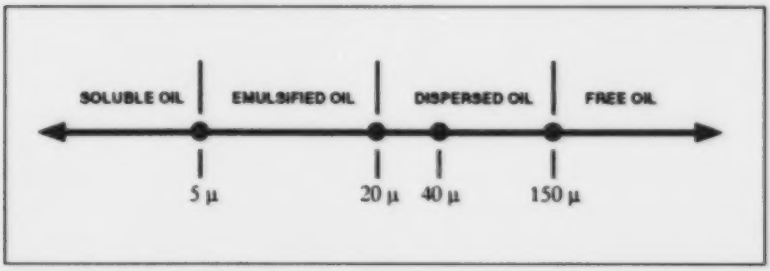

Figure 2. Oil droplet size distribution and classification.

Biological treatment has been adopted widely as the secondary treatment stage after API separation and dissolved air flotation. With this development, parameters associated with biotreatment were adopted, in addition to the oil and grease content, for classifying the wastewater composition; for example, COD, BOD, suspended solids, etc. Table 1 lists the composition of a typical waste stream after primary treatment measured by Rebhun and Galil (1987), and compared by them to values reported in the literature. [Corresponding values for the parameters after biological activated sludge treatment are also listed in the Table; these are discussed later].

The description and characterization of wastes intended for biological treatment, particularly with respect to the organic component, has traditionally been in terms of gross parameters such as BOD. Parameters such as these, although encompassing a range of individual chemical compounds, are nevertheless useful in the design and operation of biological treatment systems. These parameters also enable assessment, to some degree, of the impact of treated effluents on the receiving waters; for example, oxygen profiles in streams and rivers. However, the gross parameters provide no information on the relative amounts of different components.

Component	Influent		Effluent	
	R&G	Literature	R&G	Literature
pH	8.14	6.2–10.6	7.85	6.7–7.9
Total suspended solids	98	15–85	47	6–112
Volatile susp. solids	65		26	
COD — total	625	140–3340	230	80–300
COD — soluble	443		165	
BOD — total	268	7–230	19	4–100
BOD — soluble	143		7	
Hydrocarbons	40	23–200	4.8	0.5–9.0
Ammonia (as N)	21	0–120	13	0–43
Chlorides		19–1080		
Sulphides		0–38		

Table 1. Example of Concentrations of Refinery Wastewater Pollutants Before and After Biological Treatment (after Rebhun and Galil (R&G) 1987). [Concentration units of mg L^{-1}].

The nature and types of organic compound reflected in the BOD and COD of refinery wastewater after primary oil removal and prior to secondary treatment can be anticipated to some degree from consideration of the nature of the crude oil feedstock and the processing steps in the refinery. The "insoluble" portion (total minus soluble BOD or COD) will principally comprise free and dispersed oil (hydrocarbons) not removed in the primary treatment stage. Compounds making up a significant fraction of the soluble portion have been identified through GC/MS analyses as phenolics, short-chain carboxylic acids, naphthenic acids, and various substituted aromatics (Sun *et al.* 1987). The major sources of phenolics and short chain acids are sour water streams from the crude oil distillation process and cracking units. These oxygenated organics are thought to be derived from thermal decomposition of higher molecular weight oxygen-rich components of the oil. The concentrations will therefore depend to a degree on the oxygen content of the crude oil feedstock. The refinery processing scheme also has an influence; for example, severe hydrotreating of certain distillates has been shown to reduce phenolics concentrations in sour water (NCWQ 1975).

In recent years there has been increasing concern regarding the carcinogenic or mutagenic potential of specific compounds (and ionic species) and groups of compounds, even when present in low (trace) concentrations. This concern has lead to the compilation of the U.S. EPA's Priority Pollutants List and the Ontario Ministry of the Environment's Effluent Monitoring Priority Pollutants List (EMPPL). These lists have been used as a basis for identifying sources of pollution, assessing the pollution potential of point sources (including industrial effluents), and for formulating regulatory treatment standards. Identification of specific chemical components in effluents from petroleum refineries, usually with the lists of priority pollutants as a reference, has received increasing attention over the past decade. These efforts have been paralleled and supplemented by toxicity testing programs.

The majority of compound-specific field testing programs in the petroleum refining industry appear to have been directed at the final effluent after treatment. That is, effluents on discharge to receiving waters rather than effluents prior to primary and/or secondary treatment. The results of some of these final effluent surveys are discussed later. This approach has limited the utility of the data in that the removal performance of the on-site treatment systems cannot be evaluated. One compound-specific survey of the composition of refinery wastewater prior to biological treatment was conducted by the American Petroleum Institute (API 1984). Certain of the results are summarized in Table 2; these contaminants were found in wastewaters prior to biological treatment at average concentrations exceeding 100 ppb.

In summary, the composition of wastewater generated in petroleum refinery operations is reported on three levels of organization:

- Parameters relating to oil and grease content provide information appropriate to the analysis of primary treatment in API separators and dissolved air flotation processes.
- Gross parameters such as BOD, COD and suspended solids concentrations are useful in the context of biological secondary treatment.
- Compound-specific analyses are adopted to assess levels of toxic contaminants, usually at trace concentrations, and usually with respect to lists of identified toxic contaminants.

Nature of Contaminant	Contaminant
Inorganic	Chromium Zinc
Organic	
Volatiles	Ethylbenzene Benzene Toluene
Acid Extractable	2,4-dimethyl phenol phenol
Base-Neutrals	Anthracene/Phenanthrene Naphthalene

Table 2. Trace Contaminants Detected in Refinery treatment plant influents at concentrations exceeding 100 ppb (API 1984).

Refinery Wastewater Treatment Process Configurations

A simplified flowsheet outlining the principal steps typically employed in the treatment of a petroleum refinery wastewater is shown in Figure 3. It should be stressed that this configuration is by no means definitive or complete. For example:

- Sour water stripping is shown directly upstream of the oil removal units. In practice the strippers are integrated as a part of the refinery processing trains.
- Additional treatment units could be incorporated in the system. For instance, granular media filters may be used for removal of dispersed oils in place of dissolved air flotation units, and many configurations will incorporate an equalization stage to provide attenuation of flow and concentration variations.
- The important aspect of sludge disposal is not considered.

Despite these shortcomings, the diagram provides the basis for outlining the overall treatment process.

Figure 3 identifies primary, secondary and tertiary treatment stages. In Canada current practice usually involves only primary and secondary treatment. In the U.S. the end-of-pipe treatment model selected by the Environmental Protection Agency to define effluent

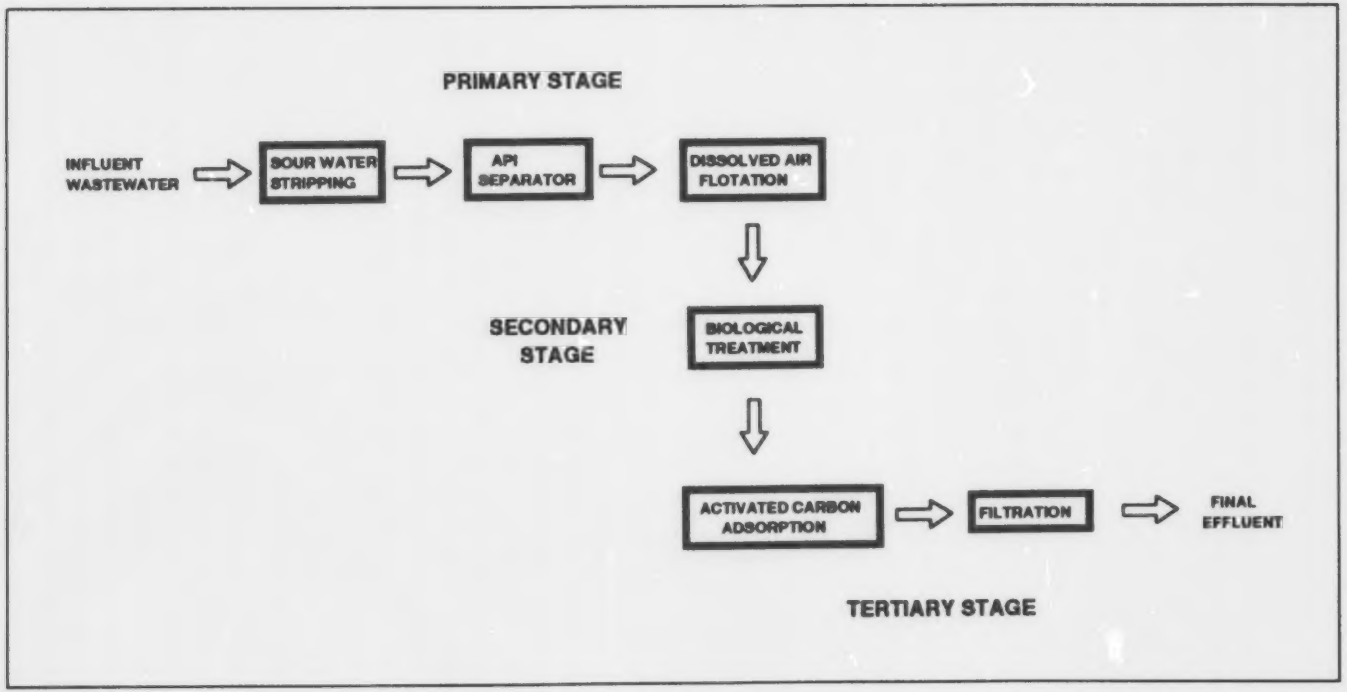

Figure 3. Typical Refinery Wastewater Treatment Process Configuration.

quality for BAT (best practicable control technology currently available) consisted of primary, secondary and tertiary treatment stages (PACE 1989). Therefore, the tertiary stage has been included in the diagram. In the following sections the primary and secondary treatment process components are discussed. The stage of biological treatment will be dealt with in more detail than the others as it is this process which has a crucial role in the removal of toxic trace contaminants.

Pretreatment

Sour Water Stripping

Hydrogen sulphide and ammonia are present in refinery wastewaters at appreciable concentrations. These are derived principally from the steps of desulphurization, nitrogen removal and hydrotreating. Streams from these refining steps are collectively called sour water condensates. It is common practice to reduce the concentrations of these pollutants through steam stripping. This operation is carried out in a reflux column equipped with either trays or a packing material.

Performance of the steam stripping process is dependent on pH, amongst other parameters. A low pH favours hydrogen sulphide removal; at low pH the ammonia is present in the ionic form. The converse is true at high pH. Performance is also very temperature dependent. Hydrogen sulphide can be stripped readily at 40°C while temperatures in excess of 100°C are sometimes applied for ammonia removal. For these reasons the stripping process is sometimes conducted in two stages to optimize performance.

Certain organics such as phenol are also removed to some degree in sour water stripping.

API Separator

The function of an oil-water liquid-liquid separator such as the API separator shown schematically in Figure 4, is to separate immiscible liquids present in a wastewater stream. Sufficient time under quiescent conditions is provided in the separator for oil droplets to coalesce and rise to the surface, forming a continuous phase of floating oil; this oil is skimmed from the surface, and thereby removed from the waste stream. The skimmed oil is recycled to the upstream refining process. Sludge accumulating at the base of the separator must be withdrawn and disposed of in an appropriate manner.

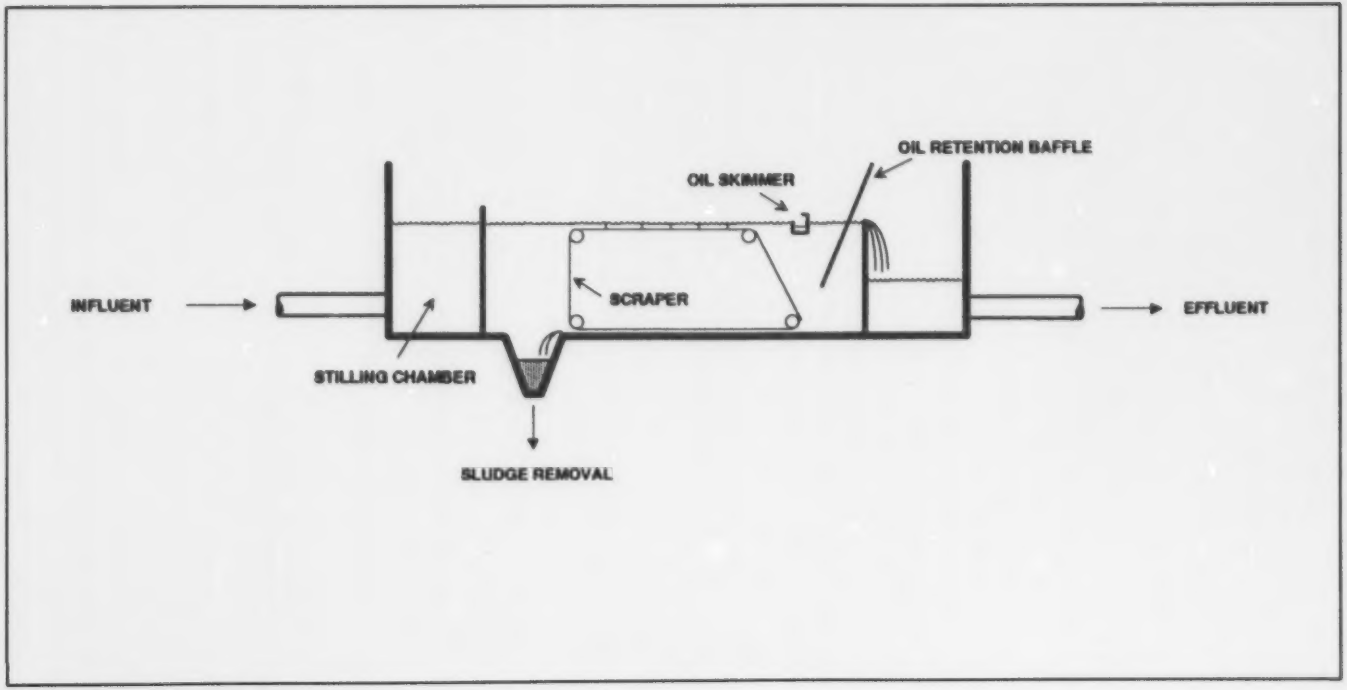

Figure 4. Schematic Diagram of API Separator Configuration.

The rate of rise of an oil droplet in water is dependent on the droplet size. Three forces act on oil droplets in suspension: buoyancy, drag and gravity. The buoyancy force is proportional to volume, while the opposing drag force depends on surface area. With increasing droplet size the volume to surface area ratio increases; therefore, larger droplets rise more rapidly and smaller droplets can remain in suspension. The API separator is designed on the basis of removing oil droplets larger than 150 microns in diameter.

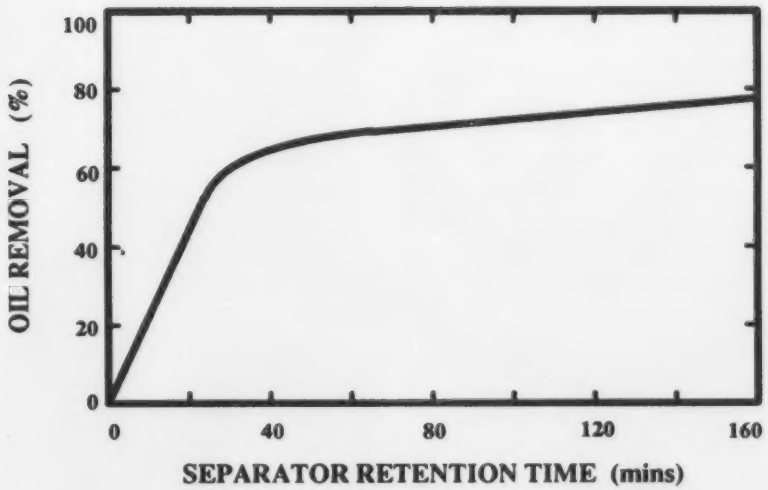

Figure 5. Influence of API Separator Retention Time on Oil Removal Performance (after Patterson 1985).

Figure 5 (Patterson 1985) shows that the oil removal performance of an API separator increases approximately linearly with retention time up to a retention time of 30 to 40 minutes. There is only a marginal improvement in performance for longer retention times.

Dissolved Air Flotation (DAF)

Dissolved air flotation is a gravity separation process in which air bubbles are attached to oil droplets. The bubble-droplet agglomerates have a density less than that of the wastewater and rise to the surface, accumulating as a "float". The "float", containing the oil droplets, is removed continuously by scraping and returned to the refinery operation. In essence, the separation process is very similar to that occurring in an API separator. The difference is that DAF is more effective in removing dispersed oil droplets because the buoyancy difference is enhanced by attachment of the small air bubbles.

The air bubbles are produced through saturating a liquid stream under pressure (at approximately 3 to 6 atmospheres); when the saturated stream enters the flotation chamber through a pressure-reducing valve the dissolved air comes out of solution as tiny bubbles. The principle of DAF can be implemented in a number of possible configurations, depending on the stream which is saturated. In general, the most common configurations involve saturating either the whole influent wastewater flow or a recycled effluent stream as shown in Figure 6.

Oil droplets greater than approximately 40 microns in size can be removed in DAF units (API 1969). Performance with respect to overall oil removal can be enhanced by the addition to the DAF influent of coagulant chemicals such as alum and ferric salts (sulphate or chloride). These chemicals have a physicochemical effect, apparently serving to demulsify and increase droplet size and to improve droplet-bubble adhesion, thereby improving net removal. Manning and Snider (1983) demonstrated that pH is a very important control parameter when coagulant chemicals are employed. For example, at the low ferric sulphate dose of 10 mg L^{-1} oil and grease removal increased from 64% to 86% when the pH was adjusted from 10.6 to 8.5.

Biological Secondary Treatment

The effluent from primary treatment contains a considerable amount of dissolved and suspended organic material in addition to any emulsified or dispersed oil which is not removed in the primary stage (see Table 1). Further treatment to remove the major portion of the organic material is generally accomplished in biological processes employing microorganisms.

In the biological process organic material serves as an energy source supporting the growth of microorganisms (principally het-

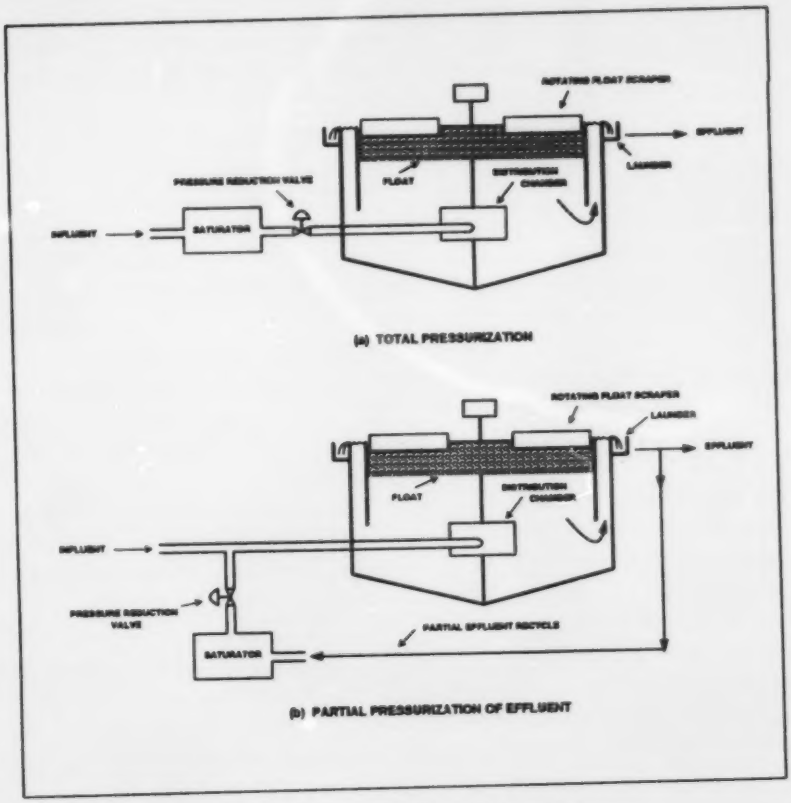

Figure 6. Schematic Diagrams of DAF Configurations.

erotrophic bacteria). The heterotrophs comprise a broad spectrum of organism species which, given sufficient time and the appropriate environmental conditions, will utilize most forms of organic material. The organic energy source serves two functions for the organisms:

(1) A portion of the organic material is oxidized, providing energy for (2); this oxidation process is called *catabolism*.

(2) Part of the energy from (1) (approximately 50%) is captured and utilized to convert the remaining portion of organic material into new cell tissue; this process is referred to as *anabolism*.

The combined process is known as *metabolism*. In the energy-generating step organic molecules are split to yield hydrogen ions, carbon dioxide and electrons; for this reason the organic compounds are sometimes referred to as the *electron donor*. The electrons and hydrogen ions are transferred via a series of reactions to a *terminal electron acceptor*. Under aerobic conditions the electron acceptor is

oxygen (which is reduced to water). The overall biochemical process may be viewed as:

$$\text{Organic material} + O_2 \longrightarrow CO_2 + H_2O + \text{New organisms} + \text{Heat}$$

As an aside, viewing the process of biological metabolism as a series of electron transfers provides justification for the Chemical Oxygen Demand (COD) as a parameter for measuring the strength of a wastewater and for analyzing biosystem behaviour. The COD test provides a direct measure of the electron-donating capacity of a waste; each mole of O_2 accepts a fixed number of electrons (four moles). As electrons cannot be created or destroyed, the mass of COD entering a biosystem per unit time must equal the sum of the mass of COD leaving in the effluent, the COD of the wasted sludge, and the oxygen utilized i.e. a mass balance is possible with the COD parameter.

The complex process of biological metabolism for the reduction of the organic content of a wastewater can be realized in a number of physical systems. These may involve a range of reactor types and configuration (plug flow, completely mixed, attached growth, etc.). Also, the process need not necessarily be aerobic; electron acceptors other than oxygen may be implicated. However, given space limitations, this discussion is restricted to the system most commonly employed in secondary treatment of petroleum refinery wastewaters; namely, the aerobic activated sludge system shown schematically in Figure 7.

In the activated sludge system a suspended microbial culture is used to treat the influent wastewater. Influent containing organic material enters a mixed reactor to which oxygen is supplied. Oxygen is generally provided by bubbling air (or pure oxygen) through the contents of the reactor (mixed liquor) from diffusers on the base as shown in Figure 7; oxygen transfer takes place at the gas-liquid interface. Alternatively, mechanical devices such as surface aerators may be utilized; mixed liquor is sprayed into the air above the liquid surface, thereby entraining and dissolving oxygen. Irrespective of the means of aeration, the rate of input is typically regulated to maintain a dissolved oxygen concentration of approximately 2 mg L^{-1} in the reactor.

The biological process taking place in the reactor essentially involves transforming organic material from the influent into a solid phase (new organisms). The microbial culture within the reactor grows in clumps called *flocs*, containing large numbers of organisms loosely bound together. The microbial culture must be separated from the liquid being treated prior to discharge of the effluent. The solid-liquid separation is usually achieved in a gravity settling tank. Under the quiescent conditions in the settler the particulate material

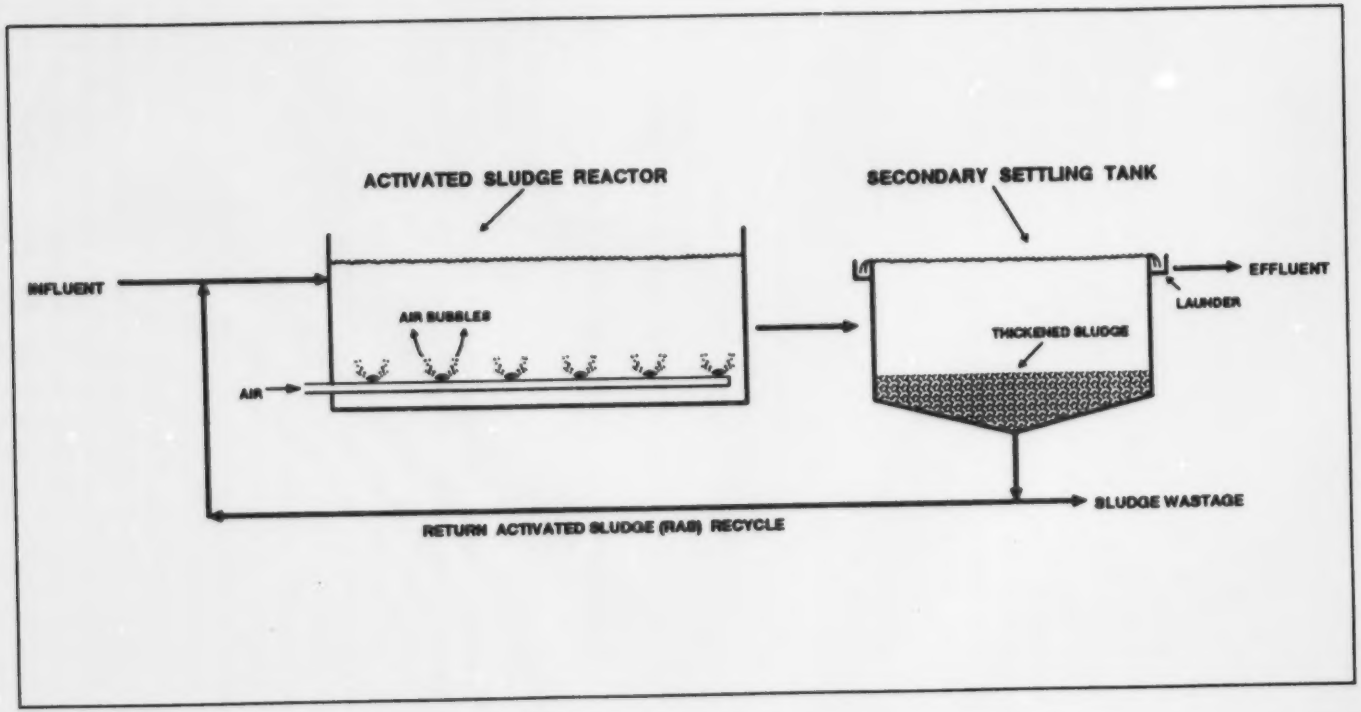

Figure 7. Schematic Diagram of Aerobic Activated Sludge System Configuration.

in the mixed liquor from the aeration tank forms relatively large flocs which settle out under gravity. Settled organism mass is returned to the bioreactor via the return activated sludge (RAS) recycle, while the clarified overflow constitutes the effluent from secondary treatment.

New organism mass is a product of the biological process. This mass is subject to processes of decay and death, as is the case with any other living matter. Particulate products of organism decay (sometimes referred to as *endogenous residue*) comprise a fraction of the solids in the mixed liquor. Therefore, it is necessary to purge solids from the system to prevent a continued accumulation and eventual failure of the system. This is achieved by removing solids from the system via the sludge wastage stream. The waste stream is usually withdrawn from the settling tank underflow where the solids concentration is greatest and therefore the volume of wasted liquor for disposal is minimized. The rate of solids wastage is the primary manipulated variable in the operation of an activated sludge system. Consider the ratio

$$\frac{\text{Mass of solids in system}}{\text{Mass of solids wasted per day}}$$

This ratio has dimensions of time, and provides a measure of the average retention time of solids in the system, assuming that the wastage rate is maintained near constant. For this reason the ratio is referred to as the *solids retention time* (SRT) or *sludge age* of the system.

Sludge age (or SRT) is perhaps the most important single parameter to be controlled in the operation of an activated sludge system. For a given influent load (product of concentration and flow rate), the sludge age largely determines the mass of solids in the system and the oxygen demand of the system. This in turn determines the system volume required to operate at a given solids concentration and the required capacity of the aeration system. Sludge age also influences the diversity of organism types making up the mixed culture of microorganisms. Because different organism types can exhibit different growth rates, as sludge age increases organisms with lower growth rates can be sustained in the system. The increasing organism diversity with increasing sludge age can improve the ability of the system to degrade organic materials which are resistant to biological breakdown and perhaps regarded as recalcitrant (unbiodegradable).

The discussion of biological oxidation above has been restricted to the fate of organic material in the wastewater. There are also certain reduced inorganic compounds which can be oxidized aerobically

by specific genera of bacteria. These bacteria are termed chemo-autotrophic; that is, they utilize inorganic compounds as their energy source and CO_2 as the carbon source for synthesis of new organism mass. Two autotrophic bioprocesses have relevance with respect to aerobic biological treatment of refinery wastewater, and can have an appreciable influence on the total oxygen requirement:

Nitrification: Ammonia-nitrogen (NH_3/NH_4^+) can be oxidized to nitrate (NO_3^-) in a two-step process. The first step involves oxidation of ammonia nitrogen to nitrite; this is followed by oxidation of nitrite to nitrate. Nitrification is often regarded as desirable in that nitrogen in the form of nitrate is less toxic to fish in receiving waters than is ammonia nitrogen. Because nitrifying organisms have low growth rates, systems must be operated at sufficiently "long" sludge ages to sustain their existence. Nitrifying organisms have been reported as particularly susceptible to toxicity; therefore sudden loss of nitrification may provide an indirect indication of the presence of excess amounts of toxic contaminants in the influent.

Sulphide oxidation: Sulphide (S^{2-}) can be oxidized biochemically to sulphate (SO_4^{2-}).

The primary objective of activated sludge treatment is the biological removal of organic pollutants in the wastewater. While the principal component of the removal is biodegradation, there are additional mechanisms which contribute to the reduction of the levels of certain materials between the influent and effluent of the activated sludge system. These are discussed briefly:

Stripping of Volatile Material:

A number of the organic components in refinery wastewater have relatively high volatilities; for example, benzene, toluene, xylenes and ethylbenzene. These are sometimes referred to generically as volatile organic compounds (VOC's), although this classification is somewhat subjective as different compounds will exhibit differing degrees of volatility as defined by Henry's Law. However, given the mixing intensity in the activated sludge bioreactor and the aeration method, volatilization can contribute substantially to the removal of certain compounds from the liquid phase. This may be desirable from the perspective of the liquid effluent quality; however, the aspect of air pollution may have important consequences.

Quantifying the extent of volatilization from activated sludge systems has been found difficult experimentally. Several factors appear to contribute to this difficulty; for example:

- Very often the compounds being investigated are present at low concentrations. Uncertainty in the accuracy of analytical techniques causes difficulties in the interpretation of experimental data. For instance, Melcer *et al.* (1989) reported mass balances ranging from 68 to 123% when studying the stripping of 15 unchlorinated and 7 chlorinated compounds in municipal activated sludge systems.
- The stripping process occurs in conjunction with other removal processes such as biodegradation and biosorption. Therefore, apportionment of the contributions of the different removal mechanisms poses difficulties (Schroder 1987; Weber *et al.* 1987).

Biosorption:

Certain organic and inorganic compounds present in refinery wastewaters can be adsorbed onto (or perhaps absorbed into) microorganisms. Three mechanisms of sorption have been identified: physical adsorption, chemisorption (also known as specific adsorption) and ion exchange. Physical adsorption occurs through the action of van der Waals forces; because the forces are weak, desorption is readily facilitated. Nonionic, nonpolar molecules such as DDT, aldrin and chlorinated hydrocarbons are taken up by physical adsorption. Chemisorption is the term describing surface complex formation where a cation is bonded to a negatively charged functional group of the complexing agent located on the microorganism surface. In ion exchange the adsorption of an ion is accompanied by the simultaneous desorption of another ion of similar charge. Because the surfaces of the microorganisms in the activated sludge process generally have a net negative charge, ion exchange principally involves movement of cations; for example, metal ions. In analyzing adsorption behaviour, the octanol/water partition coefficient (K_{ow}) has proven useful.

Most of the studies attempting to quantify sorption behaviour and identify the mechanisms implicated in the sorption process have been directed at compounds not necessarily present in refinery effluents. For example, Bell and Tsezos (1989) investigated the removal by adsorption onto a pure culture of microorganisms and a mixed culture from an activated sludge plant of five compounds: lindane, diazinon, malathion, pentachlorophenol and 2-chlorobiphenyl. In the case of malathion the sorption appeared to result from chemical reaction, and was irreversible. For the other compounds the adsorption was physical and reversible. This identifies an obvious problem in the treatment of waste sludge; the potential exists for adsorbed compounds to be returned to solution.

A number of investigations of refinery wastewater biotreatment have noted that poor sludge settleability and high effluent suspended solids concentrations are associated with higher concentrations of hydrocarbons (oil) in the influent to activated sludge systems. It has been proposed that the oil is adsorbed onto the sludge flocs more rapidly than it is utilized; the accumulation of oil is thought to form a hydrophobic coating on the floc, thereby adversely affecting the settling characteristics (Rebhun and Galil 1987; Tabakian *et al.* 1978).

Investigations of biosorption are fraught with many of the experimental difficulties encountered when investigating the stripping of VOC's. A further complicating factor is that, when a number of compounds with differing adsorptive properties are present simultaneously, the sorption behaviour can be competitive; therefore, results from single compound studies do not necessarily extrapolate to the mixed compound situation (Groff *et al.* 1989).

Bioaccumulation of Heavy Metals:

Heavy metals comprise a group of about 40 elements with specific gravities greater than 5 (Passow *et al.* 1961). Certain of the metals are essential trace elements for balanced growth of microorganisms. However, when present at higher concentrations, heavy metals can cause denaturation of protein (Sterrit and Lester 1980), thereby upsetting activated sludge system operation. When continuously exposed to excess concentrations, microorganisms can accumulate appreciable concentrations of heavy metals. Kasan and Baecker (1989) reported high concentrations of metals in activated sludge treating waste from a synthetic fuel plant; the elements were present in decreasing concentrations of Fe, Cr, Zn, Ag, Hg, Cu, Cd, Pb, Ni and Co. The potential for bioaccumulation has significant implications for the treatment and disposal of waste sludge from refinery biotreatment systems.

Heavy Metal Precipitation:

Petroleum refinery wastewaters contain appreciable concentrations of sulphides. With the exception of chromium, heavy metal sulphides are relatively insoluble; therefore the potential exists for metal sulphide precipitation in the activated sludge treatment system (as well as the primary treatment stages). The precipitants must be disposed of together with the waste sludge (and API sludge).

Experience/Problems Encountered with Activated Sludge Treatment

Experience with activated sludge treatment of refinery wastewaters has demonstrated that this option offers the means for removing a substantial fraction of the dissolved and suspended organic material from primary treatment effluent. Removals of biodegradable matter are in the region of 95% and are similar to the levels obtained in activated sludge systems treating municipal wastewater. For example, the data of Rebhun and Galil (1987) shows removals of 93 and 95% for the total and soluble BOD, respectively (see Table 1). In this respect, performance of systems treating refinery wastewaters is particularly satisfactory. Nevertheless, there are aspects where the performance does not attain the levels generally accepted as satisfactory for municipal wastewater treatment systems. For instance, the high effluent COD's and poor sludge settleability should be of major concern. In the following sections certain of these potential problems are discussed briefly.

High Effluent COD's:

The high effluent COD's and relatively low COD removal performance, together with the low effluent BOD, indicate that a significant portion of the influent organic material is not amenable to biological degradation. On the one hand, it might be argued that the high effluent COD (the soluble portion, at least) will have a minimal impact on receiving waters in that the amount of biodegradable material is small. However, it is also plausible that the effluent COD does in fact contain an appreciable biodegradable fraction, even though the measured effluent BOD is low. Consider the following argument: Identified effects such as inhibition may reduce the degradation of difficult-to-degrade compounds as well as affecting the removal of readily degradable material. In the BOD test the same effects could foreseeably occur, causing the BOD test to underestimate the amount of biodegradable material.

The argument above is perhaps supported by the observation that powdered activated carbon (PAC) addition to activated sludge systems significantly improves the COD removal performance (e.g. Weber *et al.* 1987). The effect of PAC addition is to remove certain organic components (possibly inhibitory) from the liquid phase through adsorption; if inhibitory components are in fact removed then the degree of biodegradation should improve. Whether the improved COD removal is due to adsorption alone or to a combination of adsorption and improved biodegradation is difficult to ascertain

due to the interactive effects of the various removal mechanisms occurring simultaneously. For example, addition of PAC also reduces the amounts of volatile compounds stripped to the atmosphere. Weber *et al.* (1987) reported that addition of 100 mg PAC L^{-1} influent flow did not enhance the removal of a number of target biodegradable compounds (benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, nitrobenzene). However, the removal of certain "poorly degradable and non-biodegradable" compounds was improved substantially (1,2-dichlorobenzene, 1,2,4-trichlorobenzene, lindane).

Irrespective of the validity of the above argument, the high COD levels in biotreated refinery effluents should be a major concern. One possible solution to the problem has been investigated by Bowers *et al.* (1989); this involved partial oxidation of the influent organics using hydrogen peroxide (H_2O_2) as a treatment step prior to activated sludge treatment. The residual by-products of oxidation were evaluated based on toxicity (Microtox) and biodegradability by an unacclimated activated sludge. It was found that the by-products were an order of magnitude less toxic and biodegradability improved. For example, a solution of 2,4-dichlorophenol exhibited an EC50 of 2.5% and an uptake rate by activated sludge of 3.47 mg TOC (g VSS.h)$^{-1}$ after pretreatment, relative to an initial EC50 of 0.37% and zero uptake.

Removal of Toxic Contaminants:

A number of studies have been undertaken to establish the nature and level of trace contaminants discharged by petroleum refineries in final treated effluents. For example, based on data collected to develop compliance, the EPA has concluded that trace contaminants found in the influents to biological wastewater treatment plants are generally reduced to very low levels (EPA 1977). This observation is supported in general by all the reviewed studies. Nevertheless, statistical analysis of data confirms that refinery effluents can contribute significant, albeit low, concentrations of certain priority pollutants.

It has been noted by Greenshields *et al.* (1987), and elsewhere, that care must be exercised in collating and interpreting trace contaminant data. Potential problems include:

- different sampling and analysis protocols from one study to another;
- high analytical variability;
- difficulties in interpreting concentrations close to the method detection limit of an analytical technique;
- the potential occurrence of trace contaminants in intake water to the refinery;

- variability in effluent quality not reflected by the limited sampling schedules applied in many studies; and
- the possibility of sample contamination.

Table 3 summarises the results from several databases of trace contaminants present in effluents from refinery treatment systems. These compounds were found with either a frequency of detection of 50% or greater or at concentrations exceeding 1 ppb (Greenshields *et al.* 1987; MOE 1989). It is significant to note that the heavy metals account for a major fraction of the detected contaminants. Following six months of monitoring at seven Ontario refineries, average effluent concentrations were reported to be 126 ppb for chromium, 4 ppb for copper and 753 for zinc (MOE 1989). Effluent chromium and zinc concentrations at two New Orleans refineries ranged from 30 to 240 ppb over a six month period (API 1974). Trace organic compounds frequently detected in treated effluents include phenol, benzene, toluene and naphthalene. Based on six months' monitoring at the Ontario refineries, average trace organics concentrations were 0.44 ppb phenol, 0.66 ppb benzene, 0.59 ppb toluene, 1.35 ppb o-xylene, and 0.78 ppb m- and p-xylene.

Inhibition of Biological Degradation and Shock Loading:

Operational problems in refinery activated sludge systems resulting from inhibition of microbial behaviour have been reported widely. The inhibition has been ascribed to a number of different toxic compounds; however, by far the most prominent causative compound has been identified as phenol (or its derivatives). As noted earlier, results from laboratory and full-scale investigations indicate that refinery activated sludge systems are capable of degrading many of the toxic or inhibitory compounds present in the influent wastewater. This does not obviate the fact that these compounds are inhibitory and that the existing systems must necessarily be operated at low organic loading rates (that is, long sludge ages or SRT's). In recent years there has been an increasing effort to determine the scope and applicability of biodegradation of toxic and inhibitory compounds and the optimum engineered configurations to exploit this capability (e.g. Gaudy *et al.* 1988).

Experience has shown that long periods of acclimation of the activated sludge may be necessary to develop the capacity to degrade these compounds. However, major process upsets and complete process failure can be encountered even with a well-acclimated system. Such disruptions are often associated with sudden discharges of high strength wastes. For example, Rebhun and Galil (1987) reported successful steady state operation of a pilot activated sludge

Nature of Contaminant	Effluent No. 1	Effluent No. 2	Effluent No. 3	Effluent No. 4
INORGANIC			Aluminum	Aluminum
			Arsenic	Arsenic
		Barium		
		Boron		
				Cobalt
	Chromium	Chromium	Chromium	Chromium
			Cr (Hex.)	Cr (Hex.)
	Copper	Copper		Copper
			Cyanide	Cyanide
				Molybdenum
				Lead
				Nickel
			Selenium	Selenium
		Strontium		
				Thallium
		Titanium		
		Vanadium		Vanadium
	Zinc	Zinc	Zinc	Zinc
		Zirconium		
ORGANIC				
Volatiles:		Chloroform		
				Chloro-methane
	Ethylbenzene			
		Methylene chloride		Methylene chloride
	Benzene	Benzene		
	Toluene	Toluene		
		o-,m-,p-xylene		o-,m-,p-xylene
Acid Extractable:	Phenol	Phenol		
Base-Neutrals:		Acenaphthene		
		Bis-2-ethyl-hexyl phthalate		
	Naphthalene	Naphthalene		

No. 1 — Frequency of detection $\geq$ 50% from PACE studies (Greenshields *et al.* 1987).
No. 2 — Frequency of detection $\geq$ 50% from MOE study (Greenshields *et al.* 1987).
No. 3 — Frequency of detection $\geq$ 50% from MOE MISA study (MOE 1989).
No. 4 — Average concentrations exceeding 1 ppb from MOE MISA study (MOE 1989).

Table 3. Trace Contaminants Found in Refinery Biotreatment plant Effluents with a Frequency of Detection of 50% or Greater or at concentrations exceeding 1 ppb.

system with influent total phenol concentrations of approximately 100 mg L^{-1}. However, a periodic regeneration operation of the gasoline washery, which produced a high strength phenolic waste (8000 mg L^{-1}) and increased the composite phenols concentration to over 100 mg L^{-1}, consistently caused problems in activated sludge plant operation. This, and many similar events which have been reported, identifies the need for interception and storage of sudden discharges; the stored waste can then be gradually discharged to the treatment system in a controlled fashion. This action necessarily implies cooperation and liaison between wastewater treatment staff and refinery staff.

Poor Sludge Settleability:

A common characteristic of refinery activated sludge systems is poor sludge settling properties, resulting in high effluent suspended solids concentrations. Average concentrations of 50 mg L^{-1} are reported regularly, with peaks in excess of 100 mg L^{-1} not uncommon. These values should be compared to those in municipal treatment plants where the effluent solids concentration can often be maintained below 10 mg L^{-1} consistently. Failure to improve settleability will no doubt lead to the necessity for incorporating tertiary filters at some point in the future.

The cause of poor sludge settleability has been widely ascribed to adsorption of excess amounts of oil on the sludge flocs, as described earlier. Rebhun and Galil (1987) also reported a correlation between increased effluent turbidity and shock loads of phenols. An additional factor which appears not to have been considered is the possible role of filamentous organism growth and the sludge bulking phenomenon, which can be so problematic in municipal wastewater treatment plants. Filamentous growths consist of linear hair-like chains of microorganisms; many different species have been identified in municipal plants (Jenkins *et al.* 1984). Under certain circumstances these organisms may grow profusely; the result is a sludge with poor settling characteristics. Two aspects of refinery wastewater treatment could possibly favour the excessive growth of filamentous organisms. Firstly, the aerobic activated sludge systems are operated at long sludge age; in similar municipal treatment plants so-called "low F/M" bulking is often associated with poor sludge settleability. A second aspect is the presence of sulphide in the influent wastewater; dominance of a specific filamentous organism type Thiothrix spp. is regularly associated with the treatment of septic municipal wastewaters containing sulphides. If filamentous organism growth proves to be a significant factor in the poor settleability of refinery sludges,

design methods and remedial strategies developed for addressing the municipal bulking problem should be evaluated.

Treatment and Disposal of Sludges:

Treatment and disposal of sludges generated in refinery wastewater treatment operations are not been dealt with here. However, it is worth noting the importance of this aspect in the overall treatment strategy. Treatment and disposal methods should take cognizance of the fact that these sludges may contain appreciable concentrations of toxic contaminants in the form of bioacccumulated heavy metals, metal precipitates and sorbed organics. Potential exists for the release of toxics where handling methods are not appropriate.

Closure

This paper provides a brief overview of current practice in the treatment of petroleum refinery wastewaters. The focus is principally on the role of the activated sludge system as a secondary treatment stage, with emphasis on the fate of toxic contaminants. The review is by no means exhaustive; many important factors are overlooked. For example, aspects such as the role of activated sludge system operating temperature and on-line process monitoring and control have not been considered. Also, tertiary treatment processes are not included in the discussion even though this aspect will no doubt become more important as regulations regarding effluent quality become more stringent.

The intention has been to convey the opinion expressed in the literature that current treatment technology achieves a significant reduction in toxic contaminants and other pollutants generated in the petroleum refining process. However, the full potential of treatment systems to effect removal of toxics and toxicity reduction is by no means fully understood. In addition, a number of problems associated with current treatment methods, some of which have been discussed briefly, identifies the need for ongoing investigations. The scope for improving treatment performance is very broad indeed.

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References

American Petroleum Institute (1969). *Manual on Disposal of Refinery Wastes.*

American Petroleum Institute (1984), "Refinery wastewater Priority Pollutant Study — Sample Analysis and Evaluation of Data". Publication No. 4346, Washington, D.C.

Bell J.P. and M. Tsezos (1989), "Removal of Hazardous Organic Poliutants by Adsorption on Microbial Biomass". *Wat. Sci. Tech.* **19**, 409–416.

Bowers A.R., P. Gaddipati, W.W. Eckenfelder and R.M. Monsen (1989), "Treatment of Toxic or Refractory Wastewaters with Hydrogen Peroxide". *Wat. Sci. Tech.* **21**, 477–486.

Environmental Protection Agency (1977). *Development Document for Effluent Limitation Guidelines: New Source Performance Standards and Pretreatment Standards for the Petroleum Refining Point Source Category.* EPA 440/1/82/014. EPA Effluent Guidelines Division.

Gaudy A.F., W. Lowe, A. Rozich and R. Colvin (1988), "Practical Methodology for Predicting Critical Operating Range of Biological Systems Treating Inhibitory Substrates". *J. Water Pollut. Control Fed.* **60**, 77–85.

Groff K.A., B.R. Kim and J.P. Gould (1989), "Estimating Adsorption Equilibria of Phenolics on Synthetic Resins from the Polar and Nonpolar Properties of the Molecule". *Wat. Sci. Tech.* **21**, 499–510.

Greenshields J., A. Maynard, G. Rees and W. Suboch (1987). *Environmental Contaminants in Petroleum Refinery Wastewaters: An Assessment of Current Information and a Monitoring Approach.* Study Prepared for the Joint Industry/Government Technical Committee, Petroleum Refining Sector of the Municipal Industrial Strategy for Abatement Program.

Jenkins D., M.G. Richard and G.T. Daigger (1984). *Manual on the Causes and Control of Activated Sludge Bulking and Foaming.* Water Research Commission, P.O. Box 824, Pretoria 0001, South Africa.

Kasan and Baecker (1989), "Activated Sludge Treatment of Coal-Gasification Effluent — II. Metal Accumulation by Heterotrophic Bacteria". *Wat. Sci. Tech.* **21**, 297–303.

Manning F.S. and E.H. Snider (1983). *Assessment Data Base for Petroleum Refining Wastewater and Residues.* U.S. Department of Commerce, Washington, NTIS.

Melcer H., D. Thompson, J. Bell and H. Monteith (1989), "Stripping of Volatile Organic Compounds at Municipal Wastewater Treatment Plants". Presented at the *AWM/EPA International Symposium on Hazardous Waste Treatment: Biosystems for Pollution Control.* Cincinnati, Ohio.

Ministry of the Environment (1989). *Preliminary Report for the First Six Months of Monitoring in the Petroleum Refining Sector (December 1, 1988 to May 31, 1989).* ISBN: 0-7729-6375-4, Water Resources Branch, Ontario Ministry of Environment.

National Commission on Water Quality (1975). *Water Pollution Abatement Technology: Petroleum Refining Industry.* Report prepared by Engineering-Science Inc., NTIS PB243830-01.

Passow H., A. Rothstein and T.W. Clarkson (1961), "The General Pharmacology of Heavy Metals". *Pharmacol. Rev.* **13**, 185–224.

Patterson J.W. (1985). *Industrial Wastewater Treatment.* Butterworth Publishers, Stoneham, MA.

Petroleum Association for the Conservation of the Canadian Environment (PACE) (1989). *A Summary of the U.S. Experience in Developing BAT Limits for Petroleum Refineries.* PACE Report No. 89-2.

Rebhun M. and N. Galil (1987), "Biotreatment Inhibition by Hazardous Compounds in an Integrated Oil Refinery". Proceedings *42nd Purdue University Industrial Waste Conference,* 163–174.

Rhee C.H., P.C. Martyn and J.G. Kremer (1987), "Removal of Oil and Grease in the Hydrocarbon Processing Industry". Proceedings *42nd Purdue University Industrial Waste Conference,* 143–150.

Schroder H.Fr. (1987), "Chlorinated Hydrocarbons in Biological Sewage Purification — Fate and Difficulties of Balancing". *Wat. Sci. Tech.* **19**, 429–438.

Sterrit R.M. and J.N. Lester (1980), "A Study of the Factors Which Influence Metal Removal in the Activated Sludge Process". *Sci. of Total Environ.* **16**, 37–54.

Sun P.T., C.L. Price, J.C. Raia and R.A. Balderas (1987), "Anomalies in Oil and Grease Analyses of Petroleum Wastewaters and Their Implications". Proceedings *42nd Purdue University Industrial Waste Conference,* 151–162.

Tabakian R.B., P. Trattner and P.N. Cheremisinoff (1978), "Oil/Water Separation Technology: The Options Available — Part 2". *Water and Sewage Works* (August).

Weber W.J., B.E. Jones and L.E. Katz (1987), "Fate of Toxic Organic Compounds in Activated Sludge and Integrated PAC Systems". *Wat. Sci. Tech.* **19**, 471–482.

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Management and Analysis of Data from Petroleum Refinery Wastewater Treatment Plants

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Abstract

An overview is provided of the main issues which must be addressed in managing and analyzing data from wastewater treatment facilities. The objectives of environmental data management and analysis are discussed from the point of view of both the plant operator or owner and the regulatory authority. Based on the examination of the 1985 records of flow and phenol concentrations from seven Canadian petroleum refineries, recommendations are made for improving existing databases. In analyzing environmental data to transform raw data into information, exploratory data analysis techniques should be used by engineers or operators who do not have formal statistical training. These methods employ simple statistical summaries and graphical data displays. The paper concludes with a brief discussion about future trends in environmental data management and analysis. An extensive statistical background on the part of the reader is not assumed.

Introduction and Overview

Current efforts to monitor trace contaminants in treated oil refinery wastewaters increase the need to implement systematic, clear, and consistent procedures for reporting and presenting all monitoring data. The ability to interpret trace contaminant data which is to be collected by the governments of the U.S. and Canada for regulations development will rely on information about operating procedures and the efficiency of removal of conventional pollutants.

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[2] SOHIO, Lima, Ohio

Much of the potential value of monitoring data collected from petroleum refinery wastewater treatment plants will be wasted if insufficient effort is devoted to managing and analyzing the data. To focus attention on the problems, an overview is given of the central issues which should be addressed by petroleum refinery staff in managing and analyzing both monitoring and operating data. Wherever possible, suggestions are made for improving data management and analysis practices.

Transforming Data Into Information

Considerable time and money are devoted to monitoring the performance of petroleum refinery wastewater treatment processes. Samples are collected and analyzed by laboratories for a wide variety of parameters, operators make observations about the state of the process, and signals are transmitted from on-line sensors. However, the process of collecting data does not, of itself, automatically generate information which can be used to improve operation. To be of use, data must be transformed into information. Much as a miner extracts gold from ore, information must be mined from the mass of measurements and observations collected from a treatment facility (Hunter 1988).

The path from data to information is represented schematically in Figure 1. Observations and on- and off-line measurements obtained from the treatment process are collected together to form a database. This database is managed by entering, storing, retrieving, deleting, and updating database records. The pre-eminent goal of database management is to ensure the accuracy and completeness of the data. Any ambiguity in the way in which data are entered or presented decreases the value of the data.

From values in the database, data summaries and displays are constructed to address the question: "What are the data saying?". For wastewater treatment plants, techniques for interpreting data will generally be of two broad types: calculations and plots. Summary statistics (such as means, medians, and ranges) or process parameters (solids retention time, hydraulic loadings, etc.) will be calculated and their values reported. Graphs will also be constructed and examined for trends, cycles, outliers (unusually high or low values), or the presence of relationships between variables. Process control charts are particularly helpful in assisting operators to detect changes in process conditions.

The effectiveness of data management and analysis techniques is judged by the extent to which the information generated can be used to evaluate and control treatment process performance. En-

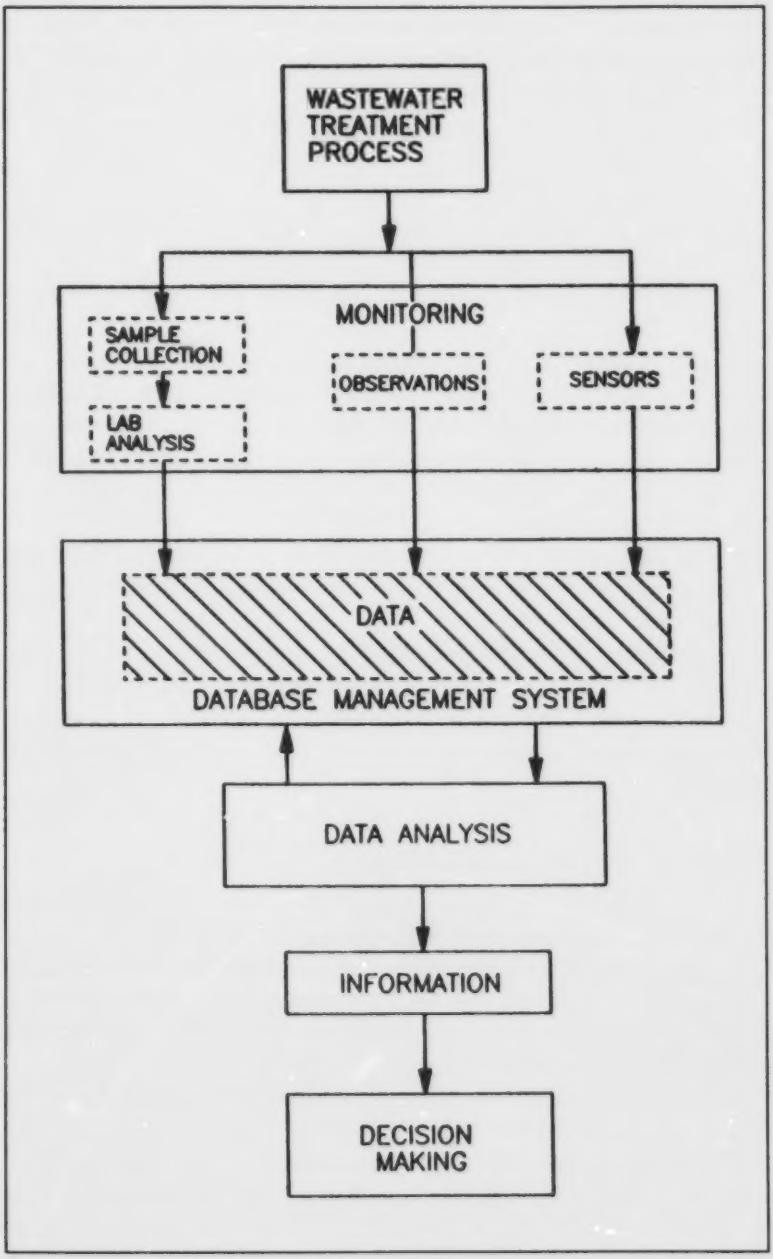


Figure 1. Schematic of Transformation of Monitoring Data to Information.

gineers and operators managing the treatment facility will use the information to:

- determine if effluent quality is within permit limits,
- optimize process performance,
- identify the need for plant modifications or expansions,
- check readings from on-line instrumentation to determine when cleaning or recalibration is required,
- as part of "community relations", to demonstrate to the public that the refinery is living up to its corporate responsibilities, and
- identify surrogate parameters for toxic trace contaminants or toxicity.

Regulatory authorities receive summary reports which are condensations of the monitoring data collected by petroleum refineries. These agencies use the information to:

- determine that the effluent quality is within limits,
- serve as basis for follow-up with the refinery should the effluent be out of compliance,
- estimate mass loadings discharged to receiving waters as part of larger efforts to determine the sources and consequences of pollution, and
- promulgate technology-based effluent regulations.

In addition, monitoring and operational data is used in special studies. For instance, as a fundamental first step in identifying process bottlenecks, consultants will evaluate the historical data collected by the plant.

The Nature of Monitoring Data

Parameters: Petroleum refinery wastewater treatment plants monitor a large number of parameters. Effluent samples are collected for a range of conventional and trace contaminants. The performance of unit processes is optimized based on observations, signals from on-line sensors, and off-line measurements.

Appendix 1 lists those conventional parameters which must generally be monitored by petroleum refineries as part of national, state, or provincial permit requirements. Attention is currently being focused on the ability of refineries to remove toxic trace contaminants. In Ontario, monitoring is underway under the MISA program for chemicals contained on the Ontario Ministry of Environment's Environmental Monitoring Pollutant List (EMPPL). In the U.S., analyses are performed on the 129 substances contained on the Environmental Protection Agency's Priority Pollutant list. All except 15 of these

chemicals are organic. Previous research indicates that the majority of substances on both lists are not present in refinery effluents (Ontario Ministry of Environment *et al.* 1987). Appendix 1 lists trace contaminants which have been frequently or occasionally detected in petroleum refinery effluents.

Measurements are also collected by plant personnel to optimize the performance of unit processes. Basic processes for the treatment of petroleum refinery wastewaters include: primary oil removal (API separator), secondary oil removal (using DAF or dual media filtration), neutralization/equalization, biological oxidation, and clarification (Ontario Ministry of Environment *et al.* 1987). Appendix 1 lists the parameters which are routinely monitored at the wastewater treatment facility operated by SOHIO in Lima, Ohio. A process schematic for the plant is given in Figure 2. Supplementing the routine measurements are observations collected by operators (Appendix 1).

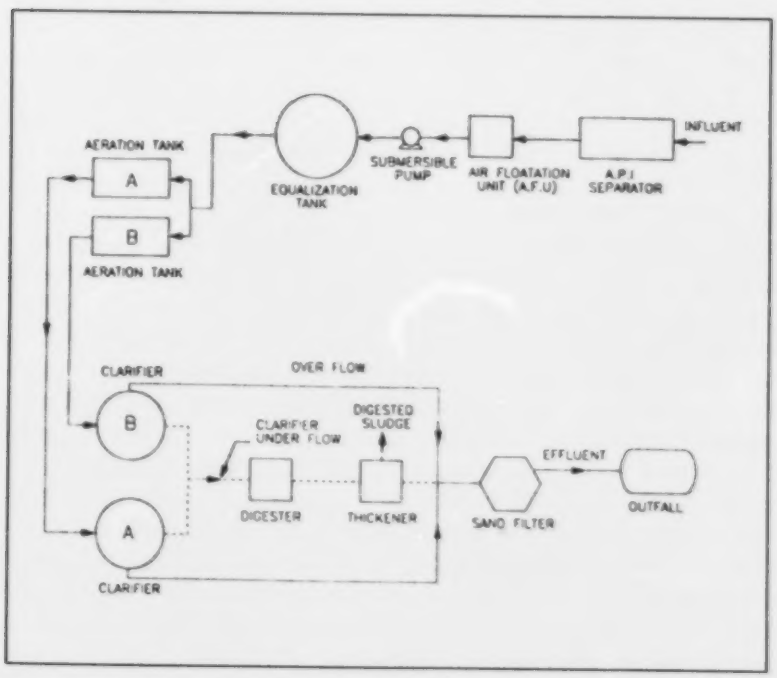


Figure 2. Process Schematic of SOHIO Refinery Wastewater Treatment Plant.

Monitoring Data Characteristics: A number of the characteristics of monitoring data make the process of information extraction dif-

ficult using conventional statistical techniques. In statistical terms, monitoring data are "messy". Frequently, values are missing or samples are collected at irregular intervals. Outliers (unusually high or low values inconsistent with general trend of the data) are often present. Monitoring data are usually skewed, histograms of the data displaying trailing tails consisting of a few high values.

Monitoring data collected more frequently than about once every three or four days are, in general, serially correlated. When data are serially correlated, high values tend to follow high values and low values low. Records of trace contaminant concentrations frequently contain "non detects" to indicate that the value was below the detection limit of the analytical technique. Detection limits are parameter specific and change with time as analytical procedures improve. The presence of "non detects" creates difficulties when calculating summary statistics such as a mean. Because most trace contaminant concentrations are present at extremely low levels (at concentrations less than 50 ppb), analytic variabilities are as high as 50% to 100% (Ontario Ministry of Environment *et al.* 1987).

Data Management

Basic Requirements

Because wastewater treatment plants collect an extensive amount of monitoring data which must be summarized and reported on a routine basis, a computer should be employed to store, organize, and manage environmental data. Basic requirements for a computerized database management system include: ease of use, ability to modify the database as monitoring requirements change, and ability to accommodate different data types.

Implementation of a computerized data management system requires careful planning. The system adopted should make it easy for operators to enter and retrieve values. Flexibility is also important. The system should be able to incorporate new sampling locations, parameters, or reporting procedures. Because of the nature of data collected from petroleum refinery wastewater treatment plants, a multi-file structure should be adopted. As discussed previously, a number of different types of data must be handled: (1) conventional effluent data, (2) trace contaminant data, (3) operational data, and (4) non-numerical observations stored in an operational log. Each type of data requires a different file structure. Common elements (such as sampling location or date) will provide links between the various files. Finally, in planning a computerized system, a phase-in

period should be adopted to give users time to develop computer skills.

Database Management Software

Commercial database management software packages can assist refineries to organize and present monitoring data. These packages are, in essence, automated filing systems. They assist users by providing features for entering, storing, retrieving, deleting, and updating records. Records can contain numbers, text, or a combination of the two. Features contained in a database manager help to maintain the integrity and security of the database.

A "forms generator" provided by a database management program is used to design the forms into which numbers or text are entered. Well designed data-input forms (which appear as display screens) minimize the time and effort needed to enter data (Chow 1987). Features can be built in to reduce typing errors during data entry. The user can be required to type in a number twice. If there is any discrepancy between the two entries, then the number is rejected (Laurie 1985). Entries into the data-input form can be checked automatically so see that they are within an acceptable range. For instance, for dissolved oxygen concentrations from aeration tanks, numbers entered into the data screen should be in the 0. to 10. mg/L range and be reported to one decimal place. Should a number be entered which does not conform to this format, the user would be asked to either re-enter the correct number or to verify the original input.

In addition to a "forms generator", database management systems contain a "report generator". A "report generator" retrieves records out of the database according to established search criteria, condenses the records, and presents results in a predetermined form. Data security is also addressed by most database management software packages. Passwords can be assigned to restrict access to certain records contained in the database. Different levels of access can be assigned so that some users can enter and modify data while others can only read the contents of the database.

A large number of commercial database management packages, with a variety of features, are available for microcomputers. Popular database management software packages include the dBase family (dBase III, dBase III Plus and dBase IV) R:base, Clipper, Paradox and DataEase (*PC Magazine* 1988). Spreadsheet packages such as Lotus 1-2-3 are frequently employed for small databases. The selection of a software package will be based on a number of factors such as the user's level of skill, compatibility with available hardware (memory, hard disk, etc.), ability of the package to import and

export data in different formats, and the size of the database. A recent issue of *PC Magazine* contains reviews of 43 such programs (*PC Magazine* 1988).

Ensuring Completeness and Avoiding Ambiguity

The first order of business in managing data is ensuring its quality and completeness (Bower 1987). Data must be entered correctly and steps taken to reduce ambiguity in the storage or presentation of results. In terms of petroleum refinery monitoring data, the following issues are fundamental to ensuring the quality of the database:

Significant decimals: The number of significant decimal places in values entered in the database should reflect the accuracy of the measurement technique. For instance, a dissolved oxygen concentration should be reported as 3.4 mg/L not 3 mg/L or 3.424 mg/L. Further, unless a refinement in a measurement technique improves accuracy, the number of decimal places should not change.

Units: Units should be reported for each parameter contained in the database, ie. mg/L for D.O. concentrations and m^3/day for flow.

Missing values: Values which are missing should be flagged in such a way that they cannot be mistaken for a measurement.

"Non detects": These values must be marked or tagged to indicate that they are below the detection limit of the method of analysis. Because they can change with time, a record should also be kept of the method detection limit (MDL).

Sample type: The database should indicate the type of sample collected. Sample types include: grabs, volume composites, flow-weighted composites, etc.

Sample location: From information contained in the database, it should be clear where the sample was collected.

Calculations: If the results of calculations are stored in the database, then the basis of the calculation should be made clear. For instance, if sludge age or SRT values are reported, reference should be made to the method of calculation.

Analysis method: The database should contain the analytical procedure which was used to generate the value. For trace contaminant data, the method detection limit should also be reported.

Zero: Zero (0., 0.0, 0.00, etc.) should only be used when a sample has been collected and no concentration has been detected using the analytical procedure. In no case is it acceptable to use zero to designate "non detects" or missing values.

Other: If trace contaminant data is stored in the wastewater treatment plant's database, then QA/QC results such as blanks, spikes, and duplicates should accompany these results. An alternative approach is to store trace contaminant and QA/QC results in the database of the analytical laboratory and cross-reference them to the plant's database using sample numbers or other identifiers.

Historical Database Problems

An examination was made of historical data consisting of the effluent volume and phenol concentration values reported in 1985 by seven Canadian petroleum refineries. As shown in Table 1, there was considerable variation in the number of values reported by the refineries.

No. of Plants	No. of Flows	No. of Phenol Concs.
3	364–365	364–365
1	355	355
1	365	345
1	365	196
1	153	153

Table 1. Number of Effluent Flow and Phenol Concentrations Reported by selected Canadian Petroleum Refineries in 1985.

A number of inconsistencies were identified in the monthly reporting sheets. A brief summary of these inconsistencies, with accompanying comments, is presented in Table 2.

The items presented in Table 2 illustrate the need for adopting systematic, clear, and consistent procedures for reporting and presenting data. Without such procedures, the quality of data is degraded and its information content is decreased. Further, the use of

Problem:	Comment:
- monthly summary states "number of data points" but the number did not correspond to the number of non-zero measurements.	- "0" sometimes representing "no available data"?
- for same plant, phenol concentrations listed as "31.24770" on one day, as "8" on others.	- inconsistent use of number of significant figures.
- values reported for phenol concentrations were identical on six consecutive days.	- same concentrations re-entered on subsequent days?
- entries listed as "NR".	- meaning?: not recorded?, not relevant?, no reading?
- entries listed as "NA".	- meaning?: not applicable?, not available?
- note on monthly summary report that "0.0 designates no sample"; some values reported as "0.0" and others as "0.000".	- confusion regarding use of zero.
- flows reported as MALPD.	- meaning?

Table 2. Problems Identified from Examination of 1985 Effluent Flow and Phenol Concentration Data from Canadian Petroleum Refineries

standardized data management procedures by all refineries is desirable so that reliable plant-to-plant comparisons can be made and an industry database created to assist in developing effluent regulations.

Data Analysis

Having ensured the accuracy and completeness of the database, an operator or engineer analyzes the data to obtain information about the performance of the plant. The nature of operational and monitoring data requires that a "bottom-up" approach be adopted to data analysis. The data should be examined in a variety of ways to determine what the data are telling us rather than imposing a "top-down" approach which subjects the data to pre-set statistical analyses. Numerical summaries and graphical displays are key components of a "bottom-up" approach.

Data Summaries

Summary statistics are calculated, in the first instance, to meet reporting requirements of regulatory authorities and, secondly, to condense and characterize a set of values. Common summary statistics computed on monitoring data include:

Range: The difference between the maximum and minimum values.

Mean: The arithmetic average of a set of values.

Geometric mean: The antilogarithm of the arithmetic average of the logarithms of a set of values. A geometric mean is used to characterize a data set which is log-normally distributed. In practice, the concentrations of most parameters in wastewater treatment plant effluents are log-normally distributed.

Standard deviation/variance: Measures of the amount of spread or dispersion of a set of values. If a data set is normally distributed, then 67% of the values will be contained within the limits defined by the mean plus or minus one standard deviation. The variance is the square of the standard deviation.

Coefficient of variation: The value of the standard deviation divided by the mean. The coefficient of variation is particularly useful for comparing samples when both the mean and standard deviation vary together.

Median: The middle value in a set of values ranked from largest to smallest.

Interquartile range: The difference between the 75th percentile and the 25th percentile in a ranked set of values. Three-quarters of the values in a data set have values less than the 75th percentile, one-quarter have values less than the 25th percentile.

Statistics such as the mean, standard deviation, and coefficient of variation are based on the assumption that a data set is normally distributed. As discussed previously, this is not the case for most monitoring and operational data. Consequently, in most cases it may be more appropriate to use the geometric mean or rank statistics such as the median and interquartile range to summarize data sets. The median and interquartile range are termed "nonparametric" as they do not assume that the data set follows any particular distribution. In addition, the value of the median is less sensitive to outliers (unusually high or low values) than is the mean.

For trace contaminant data, it is common in summarizing results to report the frequency of detection (as a percentage) and the

number of determinations. Common approaches to calculating summary statistics for records containing "non detects" involve replacing "non detects" with zero, the value of the detection limit, or one-half of the value of the detection limit. The use of such assumptions requires that they be applied in a consistent manner and that a note concerning the assumptions accompany the results. More sophisticated methods can be used to obtain summary statistics which don't require making assumptions about the values of "non detects". As a description of these techniques is beyond the scope of this paper, the interested reader is referred to Helsel and Gilliom (1986).

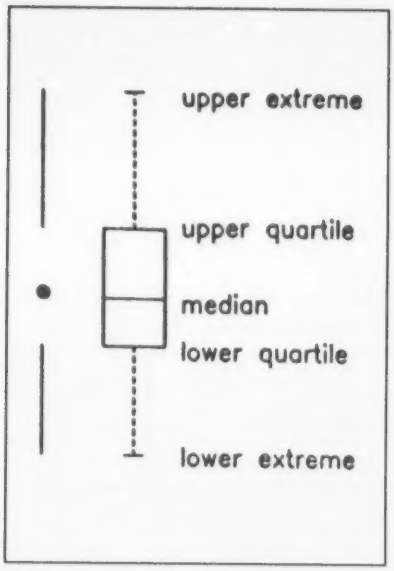
In addition to summary statistics, a variety of process calculations should be carried out using the data. Candidates include sludge age or SRT, solids and hydraulic loading rates, food/micro-organism (F/M) ratio, organic removal efficiency, oxygen transfer efficiency, polymer dosing rates, oxygen uptake rates, etc. Many wastewater treatment plants also calculate flow or mass balances to check lab measurements or flow meters.

Graphical Displays

Graphs are effective tools for presenting monitoring data. They are compact, easy to use, and draw attention to unexpected or unusual aspects of data. A description of several types of graphs which can be used effectively to display and analyze monitoring data is given as follows:

Histograms: A histogram is constructed by partitioning a data set into 5 to 20 intervals of equal length. The number of values in each interval is counted and plotted on the y-axis against the class interval on the x-axis. The histogram provides information concerning the shape of the distribution of the data set.

Box plots: The box plot is a visual display of a five number summary of a data set (Chambers *et al.* 1983). Figure 3a displays two alternative forms of the plot. The traditional box plot, shown on right of Figure 3a, consists of a box with the upper and lower edges defined by the 75th and 25th percentiles. The median or 50th percentile is the horizontal line inside the box. Vertical whiskers are extended from the upper and lower edges of the box to the maximum and minimum values of the data set. An alternative and more compact configuration is shown to the left in Figure 3a. The dot identifies the median, the solid lines the whiskers, and the resulting gap the interquartile range (the distance between the 25th and 75th percentiles).



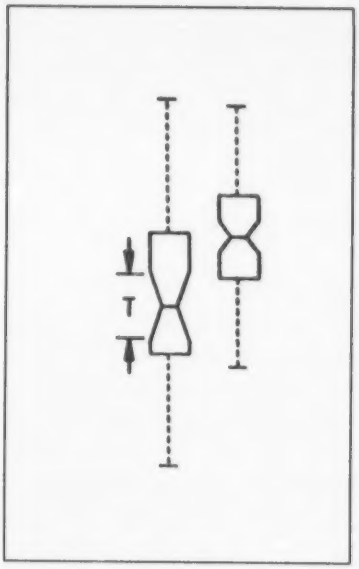


Figure 3(a). Conventional Box Plot. **Figure 3(b).** Notched Box Plot.

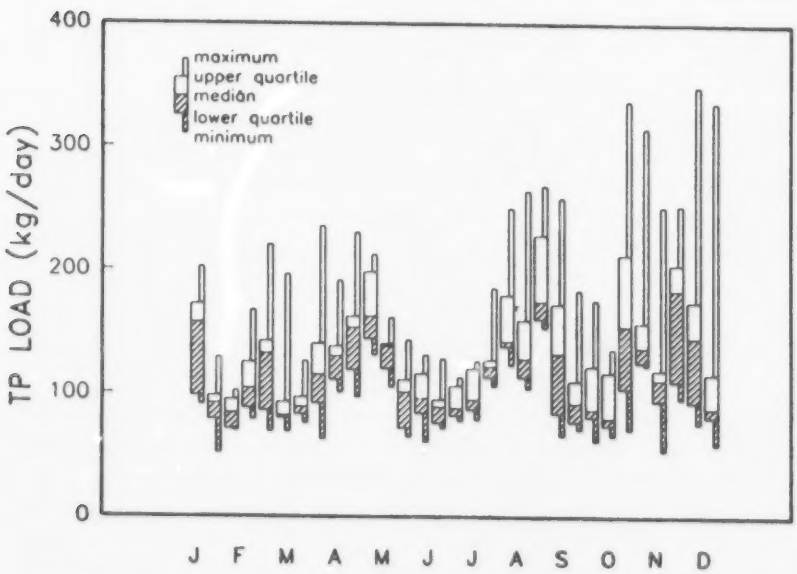


Figure 3(c). Box Plots of Partitioned Sub-sets.

In Figure 3b, a notch has been added to the box plot to indicate confidence intervals for the median. The length of the notch, T, is based on the interquartile range and the number of values in the data set (Chambers *et al.* 1983). Should the notches not overlap in side-by-side box plots (Figure 3b), then the medians are significantly different.

Box plots provide an effective and compact visual summary of a data set which has been partitioned in sub-sets (Figure 3c).

Probability Plot: Values are plotted on specially designed paper to determine if the data set follows a specific type of distribution. A data set which plots as a straight line on normal probability paper is normally distributed; plots which are not linear on normal probability paper are not normally distributed.

Scatter Plots: Scatter plots are x-y plots constructed by plotting pairs of values (x_i, y_i) with y_i on the vertical axis (ordinate) and x_i on the horizontal axis (abscissa). Scatter plots are used to study the relationships between parameters. If time is plotted on the x-axis, then a time-series plot is constructed. To help in the interpretation of x-y plots when a lot of scatter is present, smoothed curves are sometimes superimposed on the data points to indicate trend. Smoothed curves are plots of smoothed values obtained by taking the average or median of a window of points about each y_i value.

Mean Chart: Sample means are plotted with time on a graph which contains a central line representing average performance when a process is in control (Figure 4). The upper warning limit (UWL) and upper control limit (UCL) are plotted two and three standard deviations, respectively, above the historic averages. When the plotted sample means cross the UWL, it is an indication of potential problems with the process. When the plotted means cross the UCL then the plant or process is "out of control".

CUSUM Chart: CUSUMs, the sums of differences from a long-term average, are plotted against time or order of collection (Figure 5). When a plant is under control the plot of CUSUMs will be approximately horizontal and centred about zero. Should the slope of the CUSUM plot change, then a change in the process mean is indicated. Turning points, changes in the slope of the CUSUM plot, identify critical periods in plant operation when influent characteristics, operational practices or some other factor has influenced long-term performance.

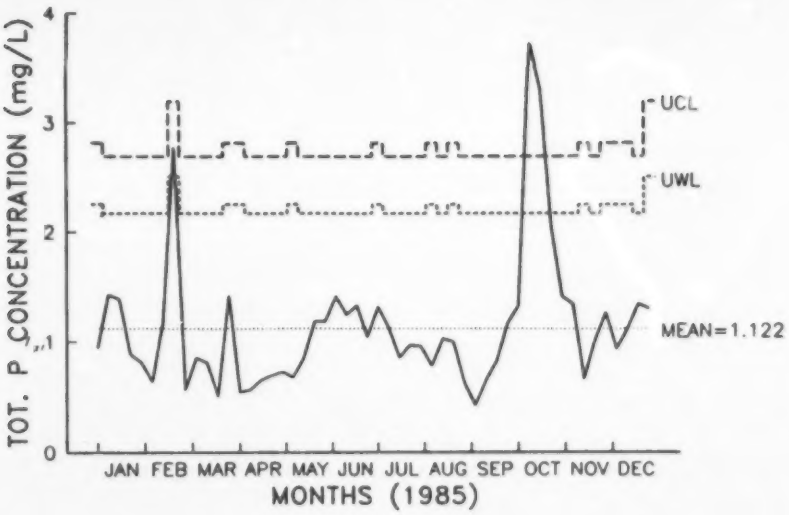


Figure 4. Control Chart for Means (Effluent Phosphorus).

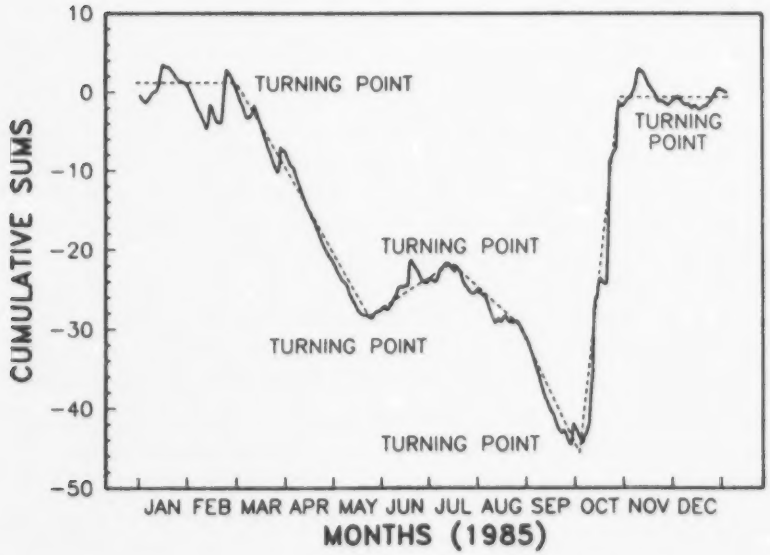


Figure 5. CUSUM Control Chart for Effluent Phosphorus.

Additional information concerning the construction and use of graphs can be found in Chambers *et al.* (1983), du Toit *et al.* (1986) or Cleveland (1985). Duncan (1986) and Fairall (1973) should be consulted regarding quality control charts.

Statistical Software

Statistical software packages facilitate the calculation of summary statistics and the generation of graphical displays. Some of the better known packages include Statgraphics, Minitab, SPS/PC, RS/1, Systat, SAS and ISML Start PC. A feature by feature comparison of 49 statistical packages is given in a recent issue of *PC Magazine* (*PC Magazine* 1989). In selecting statistical software, the user must consider compatibility with existing hardware, ability to produce a variety of graphs and summary statistics, and ease of use. Features which make software easy to use include an on-line help function, clearly written documentation, and a menu driven interface (a series of screen menus which lead the user through the procedure). In applying statistical software to the evaluation of monitoring data, the user should have some understanding of limitations and assumptions of the techniques selected.

Future Trends

Current pressures on refineries to manage, analyze, and report monitoring data will continue. In the future, there likely will be more sampling points to monitor, more parameters to be analyzed, and reporting requirements will be more rigorous. At the same time there will be more effective and sophisticated techniques available for managing and interpreting environmental data.

As previously discussed, monitoring data are frequently non-normal, serially correlated, highly skewed, and contain missing values and "non detects". Consequently, many statistical techniques based on assumptions of normality and independence cannot be applied to monitoring data. To meet this challenge, statistical techniques are emerging which have special application to environmental data. The term environmetrics — statistics in the service of the environment — has been applied to this body of knowledge. Engineers and operators will have to become more familiar with statistical techniques and terminology to take advantage of this knowledge.

There will be corresponding advances in software. Database management software will be developed which will enable graphics

to be stored and analyzed. Sampling locations can then be cross-referenced to a map or schematic stored in the database. Signal analysis will establish characteristic "finger prints" for on-line sensors. Changes in the "finger print" of the sensor with time will provide information about the need for sensor cleaning, recalibration, or maintenance.

Expert systems will be developed and applied to the management of monitoring data. Such programs are concerned with the organization and application of rules to encapsulate the knowledge of a human expert so that this knowledge can be used by a non-expert. Expert systems have the ability to handle both quantitative (numeric) and qualitative (non-numeric) information. In the future, expert systems could assist operators by analyzing a database to detect the presence of systematic long-term trends in plant performance. It is also possible that an expert system can extract rules of operation from a database. Examples of expert systems currently under development to aid in treatment plant operation are given by Berthouex et al. (1988) and Gall and Patry (1988).

Summary and Recommendations

Data should not be confused with information. Data must be managed and analyzed to extract information which can be used to optimize process performance, establish that effluent quality is within permit limits, or identify the need for process modifications.

Petroleum refineries need to implement systematic, clear, and consistent procedures for reporting and presenting all monitoring and operational data. The ability to interpret trace contaminant data will rely on information about operating procedures and the efficiency of removal of conventional pollutants. To reduce ambiguity in the way in which data are entered or presented and to lead to the development of databases with common structure and formats the following recommendations are made:

a) Data generated by petroleum refinery wastewater treatment plants should be plotted and the plots examined on a routine basis.

b) If they have not already done so, refineries should purchase the necessary computer hardware and software to manage monitoring and operational data. The conversion of manual to computer records should be implemented in phases over time.

c) The petroleum refining industry should consider adopting voluntary standards for reporting missing values, "non detects", the number of significant digits, units, etc.

d) Wastewater treatment personnel should be provided additional training in basic statistics, with particular emphasis on exploratory data analysis.

e) Following a thorough evaluation of present and future requirements, refineries should investigate the joint selection and purchase of database management and statistical software. Desirable features in database management software include: ease of use, ability to modify the database as monitoring requirements change, and ability to accommodate different data types.

f) Simplified forms or checklists should be developed to assist operators in conducting site inspections of various wastewater treatment processes. Such forms or lists would help to standardize the format of non-numeric (qualitative) records stored in petroleum refinery databases.

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References

Berthouex, P. *et al.* (1989), "A Statistics-Based Approach to Wastewater Treatment Plant Operations". *Environmental Monitoring and Assessment* **13**, 2–3, 247–269.

Bower, J. (1987) "Management of environmental information". *Pollution Engineering* **January**, 52–55.

Chambers, J.M., *et al.* (1983). *Graphical Methods for Data Analysis.* Duxbury Press. Boston. 395 pp.

Chow, B.M. (1987), "Data Bases: Getting the Most for Your Money". *Journal American Water Works Association* **June**, 56–61.

Cleveland, W.S. (1985). *The Elements of Graphing Data.* Wadsworth Advanced Books and Software. Monterey, California. 323 pp.

Duncan, A.J. (1986). *Quality Control and Industrial Statistics.* 5th edition. R.D. Irwin. Homewood, Ill. 1123 pp.

du Toit, S.H.C., *et al.* (1986). ***Graphical Exploratory Data Analysis.*** Springer-Verlag. New York. 314 pp.

Fairall, J.M. (1973), "Statistical Quality Control Charts for Wastewater Evaluation". ***Proceedings of the 28th Industrial Waste Conference.*** Purdue University.

Gall, R.A. and G.G. Patry (1988), "Knowledge-Based Systems in Wastewater Engineering". McMaster University. File No. 5-52618. 113 pp.

Helsel, D.R. and R.J. Gilliom (1986), "Estimation of Distributional Parameters for Censored Trace Level Water Quality Data". ***Water Resources Research*** **22(2)**, 135–146.

Hunter, J.S. (1988), "Decisions Under Uncertainty". Paper presented at the workshop: "Statistical Methods for the Assessment of Point Source Pollution". Burlington. September 12–14.

Laurie, P. (1985). ***Databases: How to manage information on your micro.*** Chapman and Hall/Methuen. London, 1985.

Ontario Ministry of the Environment, *et al.* (1987), "Environmental Contaminants in Petroleum Refinery Wastewaters: An Assessment of Current Information and A Monitoring Approach". A study prepared for: The Joint Industry/Government Technical Committee, Petroleum Refining Sector of the Municipal-Industrial Strategy for Abatement Program. Queen's Printer for Ontario.

PC Magazine (1989), "Statistical Software for the PC: Testing for Significance". **8**, 5, March 14, 1989.

PC Magazine (1988), "The Changing Shape of Databases". **7**, 9, May 17.

Appendix 1. Parameters Typically Monitored by Petroleum Refinery Wastewater Treatment plants

1) Parameters Monitored for Permit Compliance:
   - reported (no limits):- flow & temperature.
   - limits:- pH, oil & grease, phenols (4AAP), sulphide, total suspended solids concentrations, cyanide, phosphates, NH_3-, Nitrogen, BOD, COD, Chromium.

2) Trace Contaminants:
   - contaminants frequently detected in final effluents (Ontario Ministry of Environment, *et al.* 1987):- benzene, toluene, ethlybenzene, naphthalene, zinc, copper.
   - contaminants occasionally detected in final effluents (Ontario Ministry of Environment *et al.* 1987):- phthalate esters, polynuclear aromatic hydrocarbons, metals (antimony, arsenic, cadmium, lead, nickel).

3) Monitoring for Process Optimization:
   a) On-line Monitoring:
      - candidate parameters:- temperature, pH, flow, level, pressure, dissolved oxygen concentrations, . . .
   b) Off-Line Monitoring: Parameters designated by (*) are currently monitored at the SOHIO plant (Figure 2)
      - Air flotation unit:- oil & grease (*)
      - Equalization/neutralization tank:- COD (*), NH_3 (*), alkalinity (*), phenols (*), soluble phosphorus (*).
      - Aeration tank:- mixed liquor suspended solids concentration, mixed liquor volatile suspended solids concentration, dissolved oxygen, sludge volume index (SVI), oxygen uptake rate.
      - Final clarifier:- depth of sludge blanket, concentration of suspended solids in the return sludge, effluent suspended solids concentration.
      - Sand filters:- total suspended solids (*), alkalinity (*).
      - Equipment:-
        - blowers:- horsepower drawn, temperature, air output, output pressure;
        - pumps:- flow rates, horsepower drawn, shut-off head (centrifugal);
        - chemical feed rates.
   c) Observations:-
      - weather conditions:- wind (speed, direction), temperature, precipitation;
      - odour:- earthy, H_2S, sweet, sulpharous, other.
      - turbulence:- uniform, dead zones, blowouts.
      - foam:- extent, colour (white, brown, dark).
      - sludge settling characteristics:- floating sludge, straggler floc, pin floc, rising sludge;
      - mixed liquor microscopic examination:
        - organisms present: amoebas, ciliates, flagellates, rotifers, nematodes;
        - flocs:- shape, colour, size;
        - filaments:- description.
      - equipment status:-
      - other:-
        - algal growth on weirs or tank walls?

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Chemical Monitoring: Effective Use of Chemical Analysis for Optimization of Contaminant Removal

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Abstract

A number of comprehensive programs have been carried out to characterize oil refinery wastewaters with respect to specific organic and inorganic toxic chemicals. This paper provides some background on these studies which have shown that wastewater treatment systems at refinery sites are effective in reducing or removing toxic chemicals. Also presented is a discussion of analytical variability so readers can better appreciate the validity of results obtained from effluent monitoring programs. The variability associated with some chemical analyses, can be significant. Finally, a recommended approach towards routinely monitoring effluent quality and effectiveness of treatment, is presented. This approach involves the monitoring for total phenols, as a possible "surrogate" parameter, along with a "short list" of demonstration parameters.

Introduction

In the mid to late 70's, public awareness of toxic chemicals was increased dramatically due to media coverage of research findings on chemical spills and human exposure. For instance, the quality of drinking water in the United States came under review and studies were undertaken in which trace organic substances such as chloroform, carbon tetrachloride and other chlorinated chemicals were detected. The routine water quality monitoring programs previously carried out by the various water plants were not sophisticated enough to detect these trace substances.

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Since about 1975, environmental legislation has been drafted and enacted to deal with specific toxic chemicals and central to these legislative documents have been specific contaminant lists. The earliest comprehensive list was that published by the Environmental Protection Agency and is now referred to as the "Priority Pollutants List". Other agencies such as the International Agency for Research on Cancer (IARC) and the United Nations have also published contaminants lists reflecting the international concern over toxic chemicals.

Recently in Canada, the Ontario Provincial Government, Ministry of Environment (MOE) produced a list of 180 substances under its MISA (Municipal Industrial Strategy for Abatement) program. The Ontario MOE then enacted legislation requiring industries to monitor their effluents for the MISA list of compounds pertinent to each industry class. The legislation for the refinery sector was the first to be produced (MOE, 1988).

As a result of industry concern and the trend towards monitoring for specific environmental contaminants, the refining industry through PACE (Petroleum Association for the Conservation of the Canadian Environment) undertook a seven year series of studies concerning trace substances in refinery wastewaters (Maynard 1985). The majority of this work was completed prior to the introduction of the MISA program by the MOE. One final study was undertaken by PACE with the co-operation of the MOE (PACE 1987).

This paper will summarize the findings of the environmental contaminants projects carried out by PACE. A discussion of analytical variability is presented so readers can better appreciate the validity of analytical results. Finally, a recommended approach towards chemically monitoring effluent quality and effluent treatment will be presented. The concept of "surrogate parameters" will be discussed.

Background Information — The Characteristics of Refinery Wastewaters

Many industries in the United States responded to the new legislation through industrial associations such as the American Petroleum Institute (API) and the Chemical Manufacturer's Association (CMA). In Canada, oil refineries were studied in a series of major projects funded jointly by PACE and Environment Canada. Four field/laboratory studies plus three reviews were completed between 1980 and 1984 (Maynard 1985).

Numerous wastewater and effluent samples were analysed to characterize refinery wastewaters and assess the effectiveness of existing treatment practices in reducing trace pollutant concentrations. A total of 7 refineries across Canada, representing a cross-section of the industry, were surveyed in the first project. One of these refineries was then studied in detail to assess the variability of effluent quality. Another major program was undertaken to determine the fate and transformation of the priority pollutants within the refinery treatment systems and to determine their concentrations in refinery sludges and in air above the aeration tanks.

The most significant conclusion drawn from these studies was that present treatment systems in use at the Canadian refineries studied are effective in reducing and in some cases removing organic chemicals and metals entirely from refinery wastewaters. While a number of specific priority pollutants were found in influent waters (see Table 1), eighty percent of the contaminants on the EPA list of priority pollutants were either not detected or only rarely detected in refinery effluents.

The results of the earlier PACE studies are presented in Table 1. It can be seen that some priority pollutants were detected in refinery effluents and the summary report by Maynard (1985) recommended that the compounds listed in Section 4 of Table 1:

- benzene, toluene, ethylbenzene
- naphthalene
- phenol
- metals — zinc, chromium and copper

form the basis of a "short list" for contaminant monitoring purposes.

It should be noted in reviewing Table 1 that the high levels of benzene, toluene, ethylbenzene and phenol were from a refinery that did not have an optimized biological treatment process. This and other findings provided evidence that biological treatment was the most effective means of removing these compounds from wastewaters.

A final major trace contaminants program was undertaken by PACE in 1986 (PACE 1987). This study was undertaken in cooperation with the MOE and Environment Canada and focussed on a specific list of contaminants based on previous studies but included additional compounds from the new MISA list. It also focussed on the relationship between biological treatment and contaminant removal. The objectives of this study were threefold:

(i) to determine the relationship between trace contaminant concentrations, biotreatment plant operating conditions and refinery operation (crude throughput, shutdown and upset) for two refineries;

	Category	Contaminant or Contaminant Class	Concentration Effluent (μg/L) Min	Max	Median[c]
1.	Contaminants not detected	- Most of the Volatile Halogenated Compounds - Polychorinated Terphenyls - Polybrominated Biphenyls - Chlorophenols and Nitrophenols - Nitrosamines - Haloethers - Beryllium, Silver, Thallium			
2.	Contaminants rarely detected in influents or effluents	- Polychlorinated Biphenyls (PCB) - Hexachlorobenzene - Some Volatile Halogenated Compounds - Mercury and Selenium			
3.	Contaminants detected frequently[a] in influents and occasionally[b] in final effluents	- Phthalate Esters	ND	157	ND/1.
		- Polynuclear Aromatic Hydrocarbons	ND	13	1./ND
		- Metals (antimony, arsenic cadmium, lead, nickel)	ND	38	-
		- Cyanide	ND	140	ND/-
4.	Contaminants detected at high concentration in influents and consistently or frequently detected in final effluents	- Benzene	ND	770[d]	1./7
		- Toluene	ND	840[d]	2./1.
		- Ethylbenzene	ND	23	1/ND
		- Naphthalene	ND	59	1/1
		- Phenol	ND	900[d]	ND/1
		- Zinc	8	240	38/-
		- Chromium	2	700	9/4
		- Copper	3	37	7/-

ND = Not Detected

[a] Frequently defined as generally more than 50% frequency of detection; the 50% is arbitrary, 30% or other % occurrence could be used.

[b] Occasionally defined as generally less than 50% frequency of detection; the % used is arbitrary.

[c] Median calculated from two studies a seven refinery study, and a variability study (Maynard 1985). They were only determined for compounds or compound groups in categories 3 and 4.

[d] The maximum values of these parameters were abnormally high due to one refinery that did not have an optimized biological treatment unit.

Table 1. Priority pollutants detected and not detected in treated refinery wastewaters

(ii) to provide additional data to allow assessment of the practicability of selecting a surrogate parameter as a measure of trace contaminant removal performance; and,

(iii) to validate previous studies of trace contaminants conducted on petroleum refinery wastewaters by PACE and the API.

To meet these objectives, a sampling program was carried out at two preselected refineries in Ontario. These refineries, and their effluent treatment facilities, were considered representative in terms of the range of process complexity and the design, age, configuration, and operation of the biological treatment system.

The biological treatment plants at both refineries were demonstrated to be consistently capable of highly efficient removal of trace organic contaminants. Phthalate esters were the only trace organic compounds detected in more than fifty percent of the effluents from the biological treatment plants from both refineries. These phthalate esters, which are common plasticizers, were also found in field blank samples and have been consistently reported in all studies characterizing trace organic contaminants in municipal and industrial wastewater. Their presence in the refinery effluent samples may be associated with laboratory or field contamination. Volatile aromatic compounds, including benzene and xylenes, were identified up to 50 percent of the time of near detection limit concentrations in refinery 1 effluents but were not detected in effluents from the second refinery. The polynuclear aromatic hydrocarbons (PAHs) present in the influent to both plants were substantially removed. PAHs were not detected in any effluent samples at one refinery and only two substituted PAH compounds (dimethyl and trimethyl naphthalene) were detected in 33 percent of the effluent samples from the second refinery.

These findings are summarized in Table 2.

Analytical Variability: What Do The Results Mean

Tables 1 and 2 of this paper present a summary of a very large volume of data. Any trace contaminant program where monitoring is carried out for numerous parameters will produce a large data base. Anyone reviewing such a data base should therefore have a good feel for the variability associated with each result.

The U.S. Dept of Food and Drugs Administration (FDA) evaluate analysis procedure on the basis of three characteristics (Horwitz 1982).

	INFLUENT		EFFLUENT	
	Refinery 1	Refinery 2	Refinery 1	Refinery 2
Conventional Parameters	(mean)	(mean)	(mean)	(mean)
TKN (mg/L)	11.1	21.3	3.2	19.5
Ammonia (mg/L)	<1	19.2	<1	14.7
Phenols (μg/L)	188	22544	7.7	50.8
Oil & Grease (mg/L)	11.3	21.5	6.44	21.4
Metals (μg/L)				
As	4	43	5	44
Cd	*	*	*	*
Cr	3	270	3	280
Cu	12	5	8	7
Fe	1023	1040	161	1298
Pb	5	14	3.3	16.3
Hg	0.053	0.28	0.056	0.38
Ni	4	6	5	4
Zn	47	113	32	143
Volatile Aromatic Hydrocarbons	Mean μg/L %FOD	Mean μg/L %FOD	Mean μg/L %FOD	Mean μg/L %FOD
Benzene	73 (83)	1540 (100)	ND (50)	* (0)
Ethylbenzene	4 (50)	122 (100)	* (6)	* (0)
Toluene	27 (83)	1071 (100)	* (11)	* (0)
Xylenes	467 (100)	584 (100)	ND (44)	* (0)
Polynuclear Aromatic Hydrocarbons				
Anthracene	* (0)	* (17)	* (0)	* (0)
Methyl Anthracene	20 (100)	311 (100)	* (0)	* (0)
Acenaphthene	* (17)	* (0)	* (0)	* (0)
Fluorene	* (17)	94 (100)	* (0)	* (0)
Fluoranthene	3 (67)	* (0)	* (0)	* (0)
Naphthalene	* (0)	239 (100)	* (0)	* (0)
Dimethyl Naphthalene	58 (83)	2948 (100)	* (0)	* (33)
Trimethyl Naphthalene	79 (83)	2091 (100)	* (0)	* (33)
Phenanthrene	* (17)	127 (100)	* (0)	* (0)
Pyrene	4 (83)	* (0)	* (0)	* (0)

* No statistical analysis done
% FOD = Percent Frequency of Detection

Table 2. Comparison of selected influent and effluent contaminant concentrations

- reliability
- applicability — to a wide variety of sample types
- practicality — with respect to cost, time and training constraints

Reliability is clearly the overriding consideration and is determined by establishing a method's:

- reproducibility
- repeatability
- systematic error or accuracy
- specificity
- sensitivity or detection limit

These are listed in their approximate order of importance and each will be discussed separately.

- *Reproducibility* is the between laboratory precision of an analysis determined by inter-laboratory studies or round robins studies. It is a measure of the ability of different laboratories to check each other. Reproducibility is best expressed as a coefficient of variation (CV) which is the standard deviation around a mean, and expressed as a percent. The real aim of inter-laboratory tests is to determine how much allowance must be made for variability among laboratories in order to make the values interchangeable.

- *Repeatability* is the within-laboratory precision which defines the ability of one laboratory to check itself. It is also expressed as a CV and should be better than total variability. In most studies, within-laboratory variability is about $^2/_3$ of the total variability (Horwitz 1982).

- *Accuracy* or bias is the expression of how close a measured value is from the true value. Certain analyses can have a well defined error and this is termed a systematic error.

- *Specificity* is the ability of a method to measure an analyte without interference from other chemicals.

- *Sensitivity* is defined by the *detection limit* which is the smallest amount of an analyte that can be measured with a stated confidence. The adopted definition of sensitivity is the method detection limit (MDL) and is considered the most realistic approach to calculating a detection limit since it is based on a complete analytical procedure, includes matrix effects, and is derived from the analysis of samples or standards rather than blanks. The calculation of MDL is fully discussed by scientists from the U.S. EPA (Glaser *et al.* 1981). The MDL method has

now been adopted by EPA and the Ontario Ministry of Environment.

Analytical variability can be summarized in an oversimplified way by plotting the determined mean coefficient of variation against the concentration. (Figure 1). The sources of these data are an examination of over 150 independent inter-laboratory studies covering numerous topics from product analysis through to analysis for trace metals and pesticides (Horwitz 1982). It can be seen that the lower the concentration the higher the analytical variability. For concentrations approaching 1 ppb the variability approaches 60 percent.

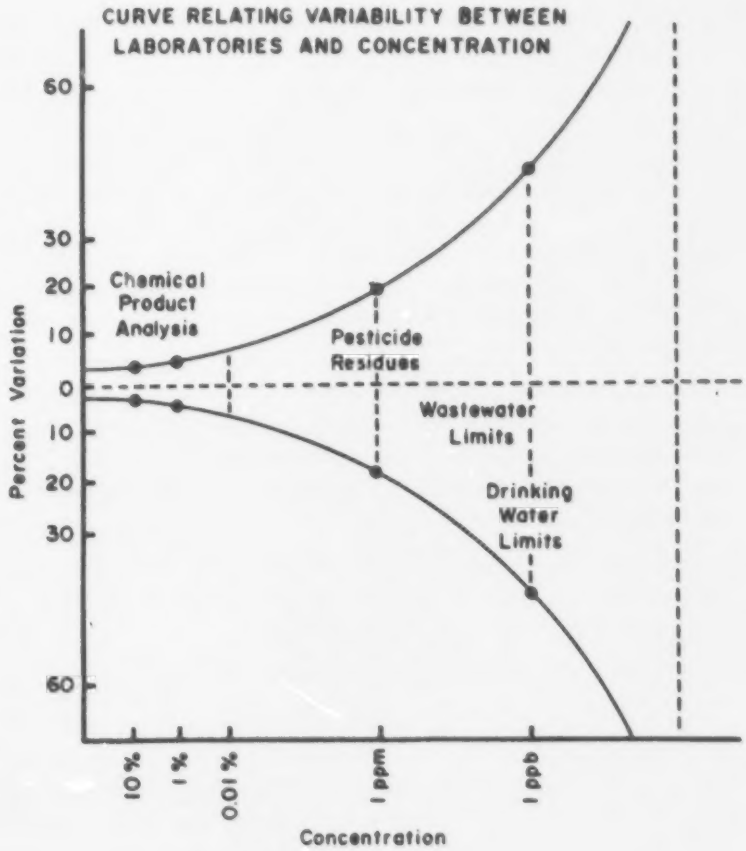

Figure 1. (Horwitz 1982)

Figure 1 represents an ideal precision curve by well established methods. There are many analyses for which the precision curve

deteriorates at the lower concentrations. There are other procedures that are specifically designed for low levels and for these the precision is good at the 1 ppb level.

Some examples of analytical variability of various environmental monitoring methods are discussed further below.

Conventional Parameters and Metals

A study was recently carried out by Maynard and Daly (1988) on behalf of PACE to investigate the inter-laboratory variability associated with certain key conventional tests used to monitor refinery wastewaters. Thirteen laboratories participated in this program. The samples consisted of blanks, synthetic samples and actual effluents. Samples were submitted blind. They were submitted to the thirteen participants on the same day and the analyses were carried out over a tightly controlled schedule.

The results indicated that the following conventional and metal tests can provide relatively precise information on an inter-laboratory basis —

Suspended Solids
Organic Carbon
Chemical Oxygen Demand, and
Metals: Chromium, Copper, Zinc

For these tests, the coefficients of variation were 15–50 percent and the number of false positives on the "blind" blanks was minimal.

For the other parameters included in the study, analytical variability is of a more serious nature. This includes:

Oil & Grease
Phenols
Ammonia

For these tests, the coefficients of variation were 46–87 percent and a number of significant false positives were reported.

Because of the problems observed with these tests, lower level results should be treated with extreme caution. There is a significant probability that a total phenols result of, say 0.004 mg/L, could indeed be zero or could be as high as 0.008 mg/L. This type of variability near the detection limit (required by the Ontario Government) of 0.002 mg/L needs to always be considered so that the detection limit itself does not incorrectly reflect data reliability. A reviewer of data must be aware of the uncertainty associated with a measurement.

Organic Parameters

With respect to organic parameters, analytical variability can be more acute especially when numerous parameters must be measured at one time. If a specific parameter or a shorter list is measured, the methodology can be more specific.

A study involving the inter-laboratory analysis for PCB in sediment was recently carried out (Alford-Stevens *et al.* 1985) with coefficients of variation ranging from 29 to 37 percent (See Table 3).

	SAMPLE 1	SAMPLE 2
MEAN (μg/g)	52.	2.7
N	20	20
SD (μg/g)	15	1.0
CV (%)	29	37.

N = number of participating laboratories
SD = standard deviation
CV = coefficient of variation
Selected results from Alford-Stevens *et al.* 1985

Table 3. PCB in sediment

EPA methods for priority pollutant monitoring are usually assessed by carrying out spike and recovery experiments. EPA contract labs are required to prepare quality assurance samples by adding or "spiking" defined concentrations of contaminants to distilled water. Four such check samples must be initially analysed followed by a routine program involving 10 percent of the sample load. The EPA published acceptance criteria for all the priority pollutants (EPA 1984) and some typical examples are presented in Table 4.

The EPA recognizes that a high degree of variability exists for certain parameters. For instance for vinyl chloride, a tolerance of more than 100 percent variability is expected. For a 20 ppb spike sample, a result from just detected (D) to 43.5 μg/L is acceptable. Benzene on the other hand, is expected to be less variable at the 20 ppb level.

While these results shown in Table 4 demonstrate high variability, a capable laboratory using a comprehensive quality assurance program, should be able to control the variation to a reasonable degree.

Parameter	Spike Level (μg/L)	Range (μg/L)
Vinyl Chloride	20	D – 43.5
Benzene	20	15.2 – 26.0
Pentachlorophenol	100	38.1 – 151.8
Phenol	100	16.6 – 100.0
Benzo-A-Pyrene	100	D – 195.
Chrysene	100	D – 134.

Selected results from EPA 1984, D = Detected

Table 4. EPA priority pollutants : recovery of spiked compounds

Recommended Monitoring Approach

Monitoring the effluent from a treatment plant is routinely required to fulfill two functions:

- To determine operating conditions
- For regulatory requirements

It would be ideal if both of these functions could be fulfilled by the same testing program but this is usually not the case. Monitoring to determine operating conditions of a treatment plant is required at a high frequency but does not usually involve many parameters. Regulatory monitoring is generally required at a low frequency and the parameter list is more comprehensive. For the MISA program, the monitoring list — even for the weekly frequency, is much more comprehensive than is needed to establish ideal treatment plant conditions.

A third function of monitoring is to demonstrate treatment effectiveness either on a continued basis or for research purposes (for example, after a treatment plant upgrade).

The Surrogate Parameter

Contaminant surveys, such as the multi-parameter programs conducted on behalf of PACE, normally have as one of the major objectives, the identification of a "surrogate parameter". A surrogate parameter is one that generally determines the quality of the effluent with respect to a long list of contaminants. If this parameter is found at a high concentration then it is assumed that other contaminants would also be present at significant levels. Ideally the sur-

rogate parameter would be a relatively straightforward conventional determination (i.e. nitrate, suspended solids, oil & grease, etc.)

To statistically establish a surrogate parameter requires that a large database be generated at varying degrees of effluent quality. The PACE studies did not identify a surrogate parameter primarily because specific contaminants were generally not detected. Therefore, statistical correlations between possible surrogate parameters and levels of specific contaminants could not be established.

The "Total Phenols" Test

One parameter which was considered a possible candidate as a surrogate parameter was "total phenols" analysed by the 4-amino-antipyrine procedure (APHA 1985). This test measures the majority of phenols found in refinery effluents. While statistical correlations could not be established, the results of the various refinery studies demonstrated that when effluent quality was poor the total phenol levels were elevated. When effluent quality was good and trace contaminant levels (i.e. benzene, toluene, etc.) were generally not detected, the total phenol levels were low (part per billion levels). These findings are consistent with the fact that phenols are biodegradable.

The majority of refineries now use the total phenols test as a tool to monitor the quality of effluent on a daily basis. Some refineries use a shortened version of this procedure (i.e. Hach Kit Methods) which is apparently effective. The shortened version procedures can be done rapidly and simply by treatment plant personnel.

A possible conflict arises when a refinery laboratory must also do daily phenol analyses to fulfill a regulatory requirement. For instance, to satisfy the MISA regulation total phenols must be done daily but a shortened version is not permitted. The test must be done following a comprehensive protocol and a full quality assurance program must be incorporated. Such a testing approach is ideal to produce good results but the procedure may not be sufficiently responsive to provide on-site monitoring of treatment performance.

One consideration would be to keep the shortened version procedure to run the frequent checks on treatment performance and maintain the records for in-house purposes only. The full procedure could then be done on samples batched from the week (i.e. 2 runs per week). These results could then be submitted for the regulation requirement.

Recommended Short List of Parameters for Demonstration of Treatment Quality

While total phenols may be a useful procedure in monitoring treatment performance, other analyses could be used to demonstrate that the treatment system is controlling toxic chemicals. The short-list previously discussed would be ideal for this purpose and is presented below with some additional discussions and suggestions.

- Volatile Aromatics — *Benzene, Ethylbenzene, Toluene, Xylenes:* These were the most frequently detected priority pollutants found in refinery wastewaters. When the concentration of these substances was low or not detected, other parameters of greater concern (i.e., polynuclear aromatic hydrocarbons) were not detected. These can be analysed using a relatively straightforward gas chromatography procedure. The recommended approach is a purge and trap isolation, capillary column gas chromatography with a photo-ionization detector.
- Key Conventional Parameters — Total Organic Carbon, Oil and Grease, Suspended Solids: If the treatment system was upset, these parameters would increase in concentration.
- Nutrients — Nitrate and Ammonia: Some treatment systems contain nitrifying bacteria and when actually nitrifying, the control of organic toxicants is good. (Melcer & Nutt 1984)
- Metals — If chromium is used in the plant then an analysis for total chromium should be routinely carried out.

In selecting any of these parameters, it is important to keep in mind the problem of analytical variability. However, for all these tests, an experienced laboratory should be able to keep the within-lab variability to within 20 percent.

Summary

From the numerous studies carried out on refinery wastewaters, it is clear than wastewater treatment systems at most refineries are effective in reducing and in some cases removing specific toxic chemicals. The monitoring carried out by treatment plant personnel involves standard conventional tests that can be completed simply and rapidly. Monitoring for specific organic and inorganic chemicals then, is required for regulatory purposes or to demonstrate effective treatment. The best candidates for such monitoring are total phenols, volatile aromatics, organic carbon, nitrate, ammonia and possibly

chromium. In utilizing data generated from such monitoring, an understanding of analytical variability is important.

Key words: Refinery wastewaters, Environmental Contaminants, Toxic Chemicals, Wastewater Characterization

References

Alford-Stevens, A.L., W.L. Budde and T.A. Bellar (1985), "Interlaboratory study on determination of PCB in environmentally contaminated sediments". *Anal. Chem.* **57(13)**, 2425–2458.

American Public Health Assoc. (APHA) (1985), "Standard Methods for the Examination of Water and Wastewater". 16th Edition, APHA, Washington, D.C.

EPA (1984), "Federal Register Part VIII Oct. 26, 1984". 40 CFR Part 136.

Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave and W.L. Budde (1981), "Trace analysis for wastewaters". *Env. Sci. Tech.* **15**, 1426–1435.

Horwitz W. (1982), "Evaluation of analytical methods used for regulation of foods and drugs". *Anal. Chem.* **54(1)**, 67A–76A.

Maynard, A.W. (1985), "A Survey of Trace Substances in Canadian Oil Refinery Wastewaters and Sludges — A Summary Report". Petroleum Association for Conservation of the Canadian Environment. Ottawa, Ontario, Report 85-8.

Maynard, A.W. and J. Daly (1988), "Interlaboratory Study to Evaluate the Analytical Variability of Conventional Parameters and Metals". Petroleum Association for the Conservation of the Canadian Environment (PACE), Ottawa, Ontario (in Press).

Melcer, H. and S.G. Nutt (1984), "The Application of Predentrification Technology for Trace Contaminant Control". *Water Sci. Tech.* **17**, 339.

MOE (1988), "The Effluent Monitoring Regulation for the Petroleum Refining Sector". Ontario Ministry of the Environment, Toronto, Ontario. July 1988.

PACE (1987), "Sampling and Analysis of Refining Effluents to Assess Variations in Trace Contaminant Concentrations". The Petroleum Association for Conservation of the Canadian Environment. Report 87-2.

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Toxicity Measurement and Reduction Procedures (Biomonitoring and TRE Programs)

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Abstract

Toxicity measurements (i.e., determining adverse effects of environmental samples on test organisms or systems) have evolved from simple acute lethality measurements with fish to more subtle measurements and are being used not just reactively (e.g., for assessment and remediation) but also proactively (e.g., in toxicity reduction and evaluation [TRE] programs). This paper outlines some of the current trends in toxicity testing and presents a phased program for TRE application to an effluent discharge. Certain limitations to toxicity testing related to regulation and an appropriate level of environmental protection are identified, in particular the fact that inter-laboratory comparisons clearly indicate that this testing provides a range of values rather than a single definitive number.

Introduction

Toxicity is operationally defined as an adverse biological effect. Detection, avoidance and elimination of toxicity are of primary concern to the public, environmental agencies, and to dischargers (who may face long-term liability if environmental problems are not identified and corrected).

Toxicity testing involves exposing an organism or biological system to a test sample (e.g., effluent, water, sediment, soil) and determining a response according to a pre-determined range of possibilities (e.g., lethal, non-lethal or of intermediate lethality). The

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simplest toxicity test involves death of the organism and is called an acute lethal toxicity test. An example would be a 96-h LC50 (lethal concentration that kills 50% of the exposed organisms) with rainbow trout. Acute testing is conducted over short time periods. More subtle toxicity tests can include chronic testing; the latter is defined as long-term effects usually involving at least one full life-cycle of the test organism. An example would be the waterflea (Daphnia) 21-day life-cycle test (APHA 1985).

In the early part of this century, most toxicity concerns related to acute lethality: specifically, there were significant parts of many water bodies in which organisms could not live due to factors such as low dissolved oxygen concentrations and high sulfide levels. Most of these problems were due to primary discharges such as sewage and pulp mills, which have now been ameliorated by secondary and other forms of treatment prior to discharge. Current toxicity concerns include acute lethality but extend to chronic effects, in particular, long-term effects on populations and individuals that do not immediately result in death. For example, while organisms now live in areas from which they were at one time excluded by acute lethality effects, some of these organisms have cancerous lesions.

The purpose of this paper is to provide a perspective on toxicity measurements as they presently exist, are being used and, in the author's opinion, should be used. Past uses have been primarily reactive (e.g., describing the extent of already existing environmental degradation); present and future uses are expected to be more proactive (e.g., determining the potential for environmental degradation and avoiding such degradation). TRE programs, which are discussed herein, are a proactive use of toxicity tests.

Toxicity Measurement

Toxicity tests can be conducted in the laboratory or in situ. They provide different but usually complementary information as compared to chemical analyses; the latter only measure contamination and provide no information on bioavailability. Toxicity tests are a form of bioassay that is effects-based and which should not be confused with bioaccumulation tests; the latter measure a phenomenon rather than an effect (Chapman 1989).

Because the environment is not a simple system toxicity tests, although they may be simple in design and implementation, provide complex information. Specifically, such tests provide information on the interaction of chemical and physical factors in complex matrices

and/or mixtures. Also, toxicity measures vary with the type of test, type of organism, life-stage, and exposure route. In other words, not all organisms are equally sensitive to all contaminants, and sensitivity can vary during an organism's life (hence the importance of chronic tests that involve a full life-cycle) and with previous exposure to contaminants (i.e., adaptation).

Toxicity testing has evolved significantly since the 1960s when the main use was reactive, in the form of data acquisition on acute toxicities. In the 1970s, acute toxicity tests were used for regulation and monitoring (i.e., both reactively and proactively); testing determined the need for source control which, once implemented, was monitored for effectiveness with toxicity tests. Presently, in the 1980s, toxicity tests are being used in hazard assessment studies. Such studies consider both toxicity and exposure (realizing that toxicity is a result of concentration and time (i.e., dose), modified by variables such as chemical form, availability, temperature, pH, dissolved oxygen and hardness or salinity), and generally involve site-specific evaluations of priority chemicals and both acute and chronic effects for non-lethal environmental samples. In the future, toxicity testing is expected to increase in importance as environmental strategies and regulations become more clearly effects-based; there is also an expectation in some quarters (e.g., Blaise *et al.* 1989) that there will be a shift from macrobiotests (e.g., fish bioassays) to microbiotests (e.g., Microtox, Chromotest and other "packaged" tests).

Partly responsible for the increasing acceptance and reliance on toxicity tests are: a realization that individual chemical criteria are not realistic; changes and renewals in regulatory policies (e.g., the Municipal Industrial Strategy for Abatement [MISA] program in Ontario; the Canadian Environmental Protection Act [CEPA]; the National Pollution Discharge Elimination System [NPDES] in the U.S.); and, the development of hazard assessment procedures as detailed above. In addition, toxicity tests are now recognized as being versatile, cost-effective, and as having good predictive potential.

Current regulatory approaches using toxicity tests involve a tiered testing approach such as the example provided in Figure 1. This approach involves conducting several tests at various levels of biological organization. The importance of conducting toxicity testing with more than one organism/test is underscored by the fact that different organisms have different tolerances to different contaminants; for instance, synoptic effluent acute lethality toxicity tests with rainbow trout and Daphnia yield cases in which all the trout die while all the Daphnia live and vise versa (Westlake 1989). Presently, fish such as rainbow trout are often used as the initial screen to determine acute lethality; under the MISA program, Daphnia acute lethality

will also be measured (Poirier *et al.* 1988). Sublethal and chronic testing (e.g., Daphnia and Ceriodaphnia life-cycle testing in freshwater; APHA 1985) is very important in the United States and should become increasingly important in Canada. Previously mentioned microbiotests may fit under initial screening or later testing and may incorporate one measure not shown in Figure 1: genotoxicity and cytotoxicity (e.g., the commercially available Chromotest).

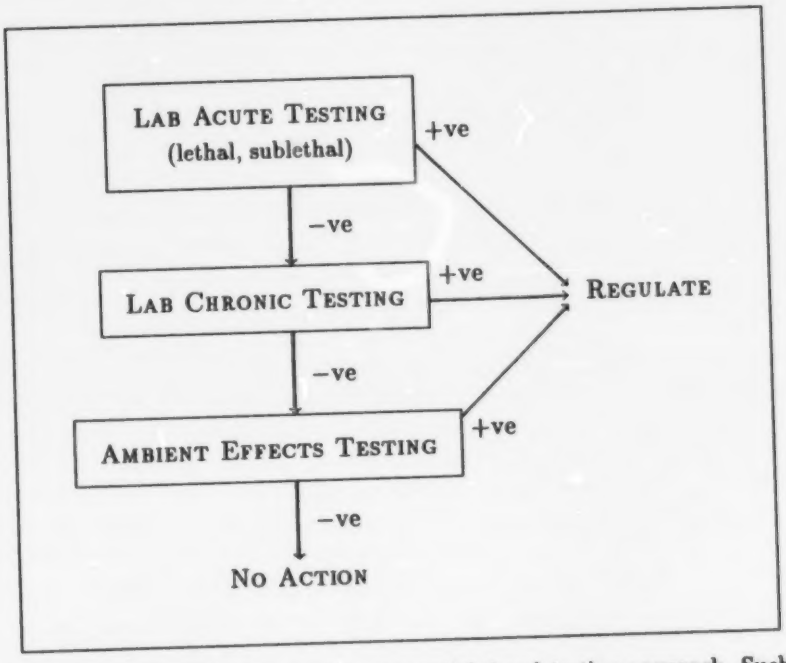

Figure 1. Example of a possible sequential tiered testing approach. Such testing should involve ecologically meaningful responses and/or allow for proactive measures. Ambient effects testing should be site-and situation-specific and could involve, for example, caged organism studies or benthic community studies.

Another evolution in toxicity testing that began in the 1970s and which came to fruition in the 1980s has been a change in the emphasis placed on particular environmental test media. Toxicity testing is no longer restricted to testing effluents and receiving waters; it now also involves testing soils and sediments. Soil and sediment toxicity tests allow determination of the toxicity of a major environmental sink and reservoir for persistent toxic contaminants, and one which can provide information on past practices that are still of environmental concern. For instance, in cases where tests of a discharge

and the surface receiving waters indicate no toxicity but the benthic community is highly altered, suggestive of anthropogenic chemical contamination, sediment tests indicating toxicity would point to an historical source. Such sediment toxicity tests can be used to delimit the area(s) of concern related to remediation.

With the increasing emphasis on toxicity tests, there has been (and will continue to be) an increase in the number and types of tests available. Moreover, the sensitivity of testing is expected to increase substantially. For instance, Environment Canada uses an ATP energy stress test with trout to determine toxicity (Blaise *et al.* 1989). However, as tests become more sensitive, their relevance to the real world and to clear-cut, meaningful changes in populations, communities and ecosystems becomes more and more problematical: the "So What?" question. While increased sensitivity is necessary to achieve an ultimate goal of proactive environmental protection (low sensitivity only allows reactive protection), it is not clear what level of sensitivity is adequate and appropriate. In other words, we must be careful that we are not so cautious and over-protective that we design and use tests that are inappropriate (i.e., result in false positives). The bottom line of environmental protection is that it must do exactly that without being overly protective such that, for instance, neither is innovation in the chemical industry inhibited, nor is society deprived of certain chemicals that may be primarily beneficial. The ultimate criteria for present and future toxicity tests are: speed, practicality, reality and cost-effectiveness.

The results of toxicity tests used, particularly for regulatory purposes, are presently not capable of producing a single numerical value; rather, a range of values is produced. Toxicity varies subtly with the exposure conditions and animals used such that inter-laboratory comparisons using synoptic samples and set protocols rarely agree within a factor of two. For instance, in a recent comparison of the Poirier *et al.* (1988) Daphnia magna 48-h acute lethality test designed for the Ontario MISA program, the variability between laboratories for four environmental samples and three reference standards varied from a factor of 2.37 to 4.20 for samples exhibiting toxicity (Chapman and Munkittrick 1989).

Toxicity tests can be used for a variety of purposes as outlined in Table 1. Because toxicity tests provide effects-based data, they are in some ways preferable to chemical analyses which provide only contamination data and no information on bioavailability or the potential effects of chemical mixtures in the real world. Toxicity tests also have advantages over in situ measurements of alteration such as benthic community structure analyses, which are subject to natural variability such that anthropogenic changes can be difficult to

detect. However, although toxicity tests are extremely useful tools, they are not perfect; in particular, such tests are limited because they are conducted under laboratory rather than real-world conditions. There are cogent reasons for using each of toxicity tests, chemical measurements and determinations of in situ alteration independently, depending on the purpose(s) of particular studies; however, a combination of each of these three methods (i.e., the Sediment Quality Triad; Chapman, In Press) provides the best overall measure of pollution-induced degradation in studies of the natural environment. For studies of discharges prior to their entry into the environment, the combination of chemical analyses and toxicity tests provides the best tool for assessment and possible remediation. An example of such combined usage is provided by TRE procedures, which are discussed below.

1. Toxicity of contaminated media (e.g., effluent, water, sediment and soil) based on level of effects for:
   - determining hazards
   - determining acceptability
   - permitting programs
   - signalling changes in environmental quality
   - dilution studies*
2. Monitoring for long-term:
   - temporal and areal changes in toxicity
   - changes after management action(s)
   - measures of the effectiveness of control measures
3. Research to:
   - determine toxic components
   - predict toxicity of discharges
   - environmental quality criteria

*Dilution studies in the case of water/effluent samples provide information on the area and extent of effects; in the case of sediment/soil studies they provide information related to possible remediation including natural and/or anthropogenic capping.

Table 1. Uses of Toxicity Tests

Toxicity Reduction (TRE) Procedures

Toxicity reduction and evaluation (TRE) procedures are discussed by Walsh and Garnas (1983) and Lankford *et al.* (1988). Standardized methods for conducting TREs have been formulated by the U.S. Environmental Protection Agency, but only the first two volumes of a series of three publications (EPA 1988; 1989) have been released.

TRE procedures serve to determine causes of toxicity in discharges, so that an appropriate treatment can be implemented to reduce toxicant concentrations for permit compliance or other purposes. TRE procedures couple effects identification (in the form of toxicity testing) with cause identification (in the form of chemical contaminant analyses). This treatment usually involves tiered toxicity testing to determine culprit chemicals or groups of chemicals that can then be eliminated and/or treated to reduce toxicity. Such testing usually involves invertebrates rather than fish for two major reasons: first, they require far less sample for testing; second, they are often considered to be more sensitive and/or to be readily amenable to life-cycle testing. In the case of freshwaters, Daphnia and Ceriodaphnia are commonly used for this purpose (EPA 1988; 1989).

If initial testing shows toxicity but an examination of all available chemical and biological data together with any information on sources contributing to the discharge does not indicate an obvious culprit, then a TRE program should be initiated. Since the overall costs for determining and remediating culprit contaminant(s) can vary from on the order of ten thousand dollars to hundreds of thousands of dollars, depending on the complexity of the problem, a tiered approach is recommended as the most cost-effective.

The success rate of TREs to date have been summarized by Steen and Wood (1988). To the end of 1988 there had been 39 major TREs in the United Stated. These included oil refineries, sewage treatment plants, chemical, metal and textile manufacturing and rubber, leather and paper plants. The culprit toxicant(s) were identified in 69 percent of cases and treatment was implemented in 54 percent of cases.

The tiered approach described below should be usable generically to indicate culprit contaminant(s). Bioassay testing is most effectively done in a range-finder mode, using Daphnia acute lethal testing (e.g., the Poirier *et al.* [1988] 48-h test) with several set concentrations and no replicates.

Tier I

Samples of the discharge should be subjected to the following procedures:

- test as is for toxicity, to establish a base-line;
- filter through a 1 mm glass fiber filter, then test for toxicity to determine if toxicity is associated with particulate matter;
- add 0.01 M EDTA to remove the EDTA susceptible cations (e.g., most metals), then test for toxicity;
- change the pH (both acidify and make basic) to test for metal-ions not reactive to EDTA (e.g., manganese), then test for toxicity;
- add 0.01 M thiosulfate to reduce free oxidants (i.e., chlorine), then test for toxicity;
- air strip for 1 hour at pH 3 and pH 11 to remove volatiles, then test to determine how toxicity varies with time;
- add powdered activated carbon to the effluent and then test for toxicity.

Tier II

If the above simple manipulations do not indicate a decrease in toxicity, then more complex solid phase extraction including the use of ion exchange resins should be conducted in an organic fractionation and characterization scheme. Portions of this scheme can also be used if the above procedures serve to decrease toxicity, but it is unclear why this reduction occurs.

Samples of the discharge should be subjected to the following procedures:

- put through a cation exchange resin, then test for toxicity;
- put through an anion exchange resin, then test for toxicity;
- put through a silica gel, then test for toxicity;
- put through a C-18 column to remove non-polar organics, then test for toxicity;

Tier III

The above described Tiers should provide information on the range or class of chemical(s) that are responsible for observed toxicity. However, if such is not the case, then additional experimental testing

may be required using a variety of organic exchange columns. Such testing represents basic research and would be directed by the results of the preceding Tiers.

Tier IV

When toxicity reduction is accomplished via any of the above Tiers, a particular range or class of chemical(s) will be implicated. The next step is to determine, as closely as possible, the particular chemical(s) involved so that treatment can be implemented. To accomplish this goal, the available chemical data should be re-reviewed, emphasizing what chemical analyses have been conducted to date on these chemical(s). Further chemical testing will thus be guided by past efforts as well as by the TRE results, including specific analytical techniques and detection limits. Following positive identification of the suspect chemical(s), then effluent that, by one (or more) of the above treatments has had toxicity removed, should be amended with the suspect chemical(s) which, if the results of the phased tiered testing are correct, will serve to restore the previously observed level of toxicity. Such a procedure provides the strongest possible evidence for chemical(s)-specific toxicity on which treatment can be based.

Conclusions

The following conclusions relate to toxicity measurements and TRE procedures:

1. Toxicity testing has evolved and will continue to evolve; it is no longer restricted to acute lethality but also includes subtle tests including chronic effects.
2. Applications of toxicity testing should involve a tiered approach which ideally includes both acute and chronic tests, different organisms, life-stages and exposure routes.
3. Toxicity testing does not produce a single unique number, but rather a value that falls within a range, ideally a range that varies by a factor of two or less.
4. Ideal toxicity tests have all of the following characteristics: speed, practicality, reality, and cost-effectiveness.
5. Although toxicity test results stand alone, they have additional value if, depending on the purpose and type of usage involved, they can be combined with either or both of chemical contaminant analyses and measures of in situ biological effects.

6. Toxicity reduction evaluations (TRE) can be conducted cost-effectively in a tiered approach, beginning with relatively simple and inexpensive generic methods.

7. Toxicity tests are no longer only used reactively but also proactively; this shift in usage involves an increased sensitivity of testing which has some danger of producing false positives but which, if used intelligently (i.e., TRE programs), can be of ultimate benefit to all environmental users including dischargers.

Key words: Toxicity, Bioassay, Toxicity Reduction Evaluation

References

APHA (1985), "Standard Methods for the Examination of Water and Wastewater". APHA/WPCF/AWWA, Washington, D.C.

Blaise, C., G. Sergy, P. Wells, N. Bermingham and R. van Coillie (1989), "Biological testing — development, application and trends in Canadian Environmental Protection laboratories". (In Press).

Chapman, P.M. (1989), "A bioassay by any other name might not smell the same". *Environ. Toxicol. Chem.* **8**, 551.

Chapman, P.M. (In Press), "The sediment quality triad approach to determining pollution-induced degradation". *Sci. Total Environ.*

Chapman, P.M. and K. Munkittrick (1989), "Inter-laboratory comparison of the Daphnia magna acute lethality bioassay". Report prepared for the Ontario Petroleum Association, Willowdale, Ontario.

Lankford, P.W., W.W. Eckenfelder Jr. and K.D. Torrens (1988), "Reducing wastewater toxicity". *Chem. Engineering* November 07, 1988.

Poirier, D.G., G.F. Westlake and S.G. Abernathy (1988), "Daphnia magna acute lethality toxicity test protocol". Ontario Ministry of the Environment. ISBN 0-7729-3798-2, 11 pp.

Steen, A.E. and S.G. Wood (1988), "Toxicity identification and reduction evaluations". Poster presented at the Ninth Annual Meeting of the Society for Environmental Toxicology and Chemistry, November 1988, Arlington, Virginia.

U.S. EPA (1988). Methods for Aquatic Toxicity Identification Evaluations. Phase I. Toxicity Characterization Procedures.

U.S. EPA (1989) Methods for Aquatic Toxicity Identification Evaluations. Phase II. Toxicity Identification Procedures.

Walsh, G.E. and R.L. Garnas (1983), "Determination of bioactivity of chemical fractions of liquid wastes using freshwater and saltwater algae and crustaceans". *Environ. Sci. Technol.* **17**, 180–182.

Westlake, G. (1989), "Applications of toxicity testing and effects monitoring". In: *Biology in the New Regulatory Framework for Aquatic Protection*. Proceedings of a workshop held April 26–28, 1988, Aliston, Ontario. (In Press).

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Online Instrumentation of Petroleum Refinery Wastewater Treatment Plants

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Abstract

Several online analytical instruments are commercially available to allow continuous monitoring of petroleum industry wastewater treatment plants. Satisfactory usage of these instruments requires special attention for sample preconditioning and sample characterization prior to selection. Specific examples of the available instruments are provided. Effective maintenance of instruments is emphasized.

Introduction

During the past few decades many concerns have been raised about water quality management, and significant resources have been directed towards the construction of municipal and industrial wastewater collection and treatment systems. The petroleum refining industry has generally provided relatively advanced treatment of the wastewaters generated by their operations. Today, however, considerable pressure is being placed on the industry to provide for the monitoring and control of toxic contaminant discharges. In Ontario, for example, this means implementing a comprehensive monitoring program and, ultimately, the best available pollution control technology economically achievable. In this connection, one of the aims of the industry is to maximize the performance of existing treatment facilities to achieve these requirements.

Past experience, particularly in municipal treatment facilities, has shown that one of the major factors limiting plant performance was the application of measurement concepts and testing to operational monitoring and process control. Plant structural and mechanical design were not always conducive to effective operational control.

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Plant operational measurement and control methods are governed by time consuming and time delayed laboratory analytical results and by operator observation of process performance. One approach to improving this situation and maximizing plant capacity and performance is through the selection and application of available online instrumentation for continuous plant monitoring and control.

Online Measurements in Wastewater Treatment

Most wastewater treatment systems have been designed and operated with a minimal amount of process instrumentation. Instrumentation actually in use is weighted towards the detection and measurement of liquid level and flow rate. Holmstrom and Hultman (1981) reviewed the usage of wastewater instrumentation in 30 plants in Sweden. They reported that 77.5 percent of the instruments were used for level and flow rate measurement; only 22.5 percent of the instrumentation was of an analytical type. The US Environmental Protection Agency (Molvar *et al.* 1976) surveyed the online instrumentation at 50 wastewater treatment plants that were known to be at least partly automated. This survey showed that in these plants only 29 percent of the installed instrumentation was analytical. The balance was flow related.

Analytical (wet chemical) instrumentation for wastewater treatment generally measures an intensive property of the treatment process, ie. concentration. Table 1 lists several analytical instruments which have been used or proposed for monitoring purposes. Most of the variables listed in Table 1 have historically been analyzed based on manually collected grab or composite samples. The sampling techniques and the inherent time delays are not conducive to the detection of dynamic disturbances nor to effective control. Today, however, instrumentation is available to measure these variables online where such measurements are warranted and when the instrumentation is applied properly.

Previous experiences with instrumentation for the measurement of analytical and physical process variables have been mixed. The Swedish (Holmstrom and Hultman 1981) and US studies (Molvar *et al.* 1976) summarized the performance of the installed instrumentation, showing that 30 to 40 percent was less than satisfactory. Usually, adverse process conditions or, in the US case, poor instrument maintenance were the causes of poor performance. In the US survey, 30 percent of instruments and/or associated automatic control loops were abandoned because of inadequacy in the instrumentation or its usage.

Variable Measured	Principle
NH_3-N	Gas sensing electrode; colourimetric, selective ion
NO_3-N	Colourimetric
Cl_2	Amperometric; colourimetric
Dissolved O_2 (DO)	Galvanic or polarographic electrode
pH	Electrode
Suspended Solids (SS)	Photometric (optical)
Sludge Blanket Depth	Photometric (optical)
Temperature	Resistance, thermocouple
TOC	Combustion or UV decomposition with IR detection of CO_2 generated
PO_4-P	Colourimetric; titration
Respiration Rate	Pressure, CO_2 absorption
ORP	Electrode
Phenolics	Colourimetric
H_2S	Colourimetric; titration; electrode
Oil-in-Water	Photometric

Table 1. Typical analytical instruments available for monitoring and control

Knudsen (1985) summarized the experiences of wastewater treatment facilities with online instrumentation for analytical and physical variables. His findings indicated that users had varying experiences with instrumentation. In general, users of analytical-type instrumentation for DO, SS, Cl_2, and pH were roughly split between those satisfied and those who were unsatisfied with instrument performance. Reported causes of dissatisfaction with performance were:

- Excessive maintenance
- Bad installation
- Could not calibrate flow meters
- Difficult maintenance due to poor installation
- Unreliable probes
- Inappropriate instrument
- Fouling

Clearly, instrumentation and application limitations need to be solved to promote acceptance of more advanced analytical equipment in wastewater treatment than exists now. The reviews by Knudsen (1985), Holmstrom and Hultman (1981) and Molvar *et al.* (1976) do suggest that many instruments are used satisfactorily for monitoring and control. In general, the less complex the instrumentation, the higher the likelihood that successful usage is experienced.

Knudsen *et al.* (1985) listed dominant reasons for unsatisfactory instrument performance. These included:

- Misapplication
- Misinstallation
- Improper maintenance

It is informative that the instruments themselves appear to be less prone to induce unsatisfactory performance than their installation and maintenance. This indicates that designers of wastewater treatment facilities need to be more cognizant of these problems to overcome the lack of confidence in instrumentation systems which have developed over the years. Considerations for successful application and usage of online instrumentation must be made in the process predesign stage. Neglect of this can lead to dissatisfaction. Investments in instrumentation systems will be wasted and reinforce negative feedback about these systems.

Manning and Dobs (1979) identified several major reasons for the failure of I&C systems in wastewater facilities:

- Lack of knowledge and expertise concerning the application of instrumentation and automation in the sanitary engineering profession.
- Lack of understanding of the correct techniques of process control on the part of design engineers and others.
- Misapplication of otherwise acceptable instrumentation.
- Lack of acceptable instruments.
- Inadequate maintenance of instrumentation.
- Lack of identified proven control strategies.
- Poor coordination between engineering disciplines involved in wastewater treatment system design.

Faults in the design and application of instrumentation systems in the wastewater industry are interactive and must be addressed simultaneously by those who design, regulate, and operate these plants.

Rationale for Online Monitoring

Petroleum refinery wastewater systems are under increased pressure by regulatory jurisdictions for the monitoring and control of

trace contaminant discharges. Specific goals of online monitoring systems in wastewater treatment facilities include, for example:

- Improvement of the degree of protection afforded to the more sensitive unit processes of the treatment plant through online monitoring of selected key contaminants and toxics in raw wastewater.
- Timely measurement of basic operating parameters in the treatment system including in-plant pretreatment systems.
- Implementation of feedback control for critical treatment plant operational parameters.
- Continuous monitoring of key effluent parameters.

Sample Conditioning

Analytical (wet-chemical) instrumentation is relatively sophisticated in design and operation. Shortcomings of instrument systems are often related to poor installation or inadequate sample conditioning which allows rapid fouling or deteriorates the performance of the sensing element. Adequate sample conditioning is needed to minimize sensor down-time and reduce maintenance requirements as much as possible. Unfortunately, relatively little can be done to protect immersed sensors such as DO, SS, pH, etc. For wet-chemical sensors, preconditioning equipment is available.

The major concern in refinery wastewater is oil and suspended solids, particularly in the untreated or partially treated waste streams upstream of the activated sludge system. Oil and grease will coat unprotected electrodes (DO, SS, ammonia, sulphide, pH) and foul visible and monochromatic light-based sensors (colourimeters and turbidimeters). Suspended solids will plug analyzer tubing and lead to failure. Adequate sample conditioning is a critical component in an online instrumentation system.

Experience has shown that effective sample conditioning prior to wet-chemical analysis is essential. Tubular ultrafilters are effective in this regard. These are flow-through devices which produce a small permeate stream for analysis. Pressure is the driving force for separation. In ultrafiltration, suspended material and high molecular weight components in the feed stream are rejected while ionic and low molecular weight components can pass through the membrane. An ultrafilter should not remove the dissolved components in the wastewater which are to be measured by online chemical analyzers. Flow rate through an ultrafilter is high and sample transport

lag times are minimized. Ultrafiltration systems are commercially used for oil/water separation. High fluid velocity tends to minimize or prevent membrane fouling in tubular ultrafilters necessitating a recirculation tank system. Table 2 shows typical performance characteristics for a tubular ultrafilter at an API settler influent location of an integrated oil refinery. In general, oil and grease and SS are effectively removed. Similar results are shown for a desalter unit in Table 3.

Parameter	Feed (mg/L)	Permeate (mg/L)	Removal (%)
Oil and Grease	58	7	80
Suspended Solids	79	6	91

Table 2. API settler sample conditioning with tubular ultrafilter

Parameter	Feed (mg/L)	Permeate (mg/L)	Removal (%)
Oil and Grease	114	17	85
Suspended Solids	6	3	55

Table 3. Desalter sample conditioning with tubular ultrafilter

Most parameters of interst for online analysis are not removed by ultrafiltration. However, parameters physically associated with rejected materials will be removed. Regardless of the stream being measured, it is strongly recommended that sample preconditioning by ultrafiltration or equally effective mechanisms be specified.

Sample Characterization

Prior to the selection and application of online instrumentation, wastewater characterization is necessary for each stream. Characterization data may be available from refinery operating records or

require special effort to define. Typically required characterization parameters include, for example:

- Typical range of parameter interest
- Minimum and maximum
- Sample temperature
- pH
- Total dissolved solids (TDS)

The necessity to reduce interfering contaminants such as oil and grease and particulates can be verified. These are critical details to be addressed prior to specifying online instrumentation.

Prerequisite Measurements in Activated Sludge Wastewater Treatment

For activated sludge process operation and control, the prerequisite measurements include flow rates (feed, recycle, waste), activated sludge settleability, suspended solids concentration (mixed liquor, recycle, effluent) and dissolved oxygen concentration. Other measurements may also be appropriate including, for example, pH and nutrient concentrations.

Suspended Solids

Suspended solids concentration is important for several reasons, including:

- monitoring and control of the biological solids inventory in the activated sludge process
- monitoring and control of effluent quality

Reliable online instrumentation is available for measurement of the high concentrations of suspended solids encountered within aeration tanks and return/waste activated sludge streams. In general, these are optical instruments which must be calibrated to laboratory results over the measurement range. This is usually adequate for the higher concentration range. For the lower suspended solids concentration range encountered in raw wastewater, primary or secondary effluent streams, calibration of online suspended solids instrumentation requires more care. This results because of the small range of the measurement and the potential changes in sample optical characteristics in these dilute suspensions. Nevertheless, useful measurements can be obtained.

Figure 1 shows the response of a calibrated final clarifier effluent suspended solids instrument to a change in plant influent flow rate. Manual grab samples and composite samples would not show the true process response and variability to input disturbances. The impact of induced disturbances, e.g. pump stations, on plant operations can be detected by online measurements. Furthermore, plant failures can be detected effectively by online measurements of effluent SS. These failures may be clarification or thickening failures.

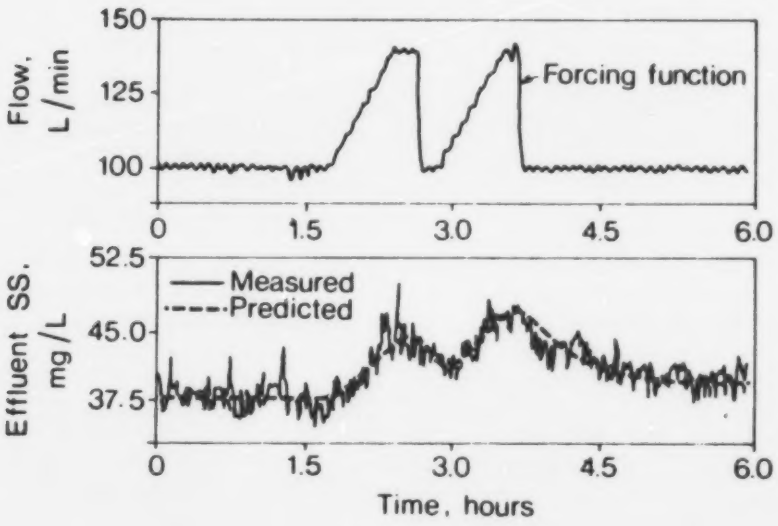

Figure 1. Online effluent suspended solids response to variation in settler flow rate.

Figure 2 shows the response of a mechanically self-cleaning suspended solids instrument to variations in influent (primary effluent) suspended solids concentration. The continuous online measurement is compared to gravimetric suspended solids determination in grab samples in the figure. The instrument reflected the trend but not the absolute concentration. This difference was attributed to instrument drift.

Secondary clarifier effluent SS concentration data are also shown in Figure 2. The effluent data represent continuous and grab sample (gravimetric) results for two parallel activated sludge plants receiving common primary effluent feed. Settleability in one of these

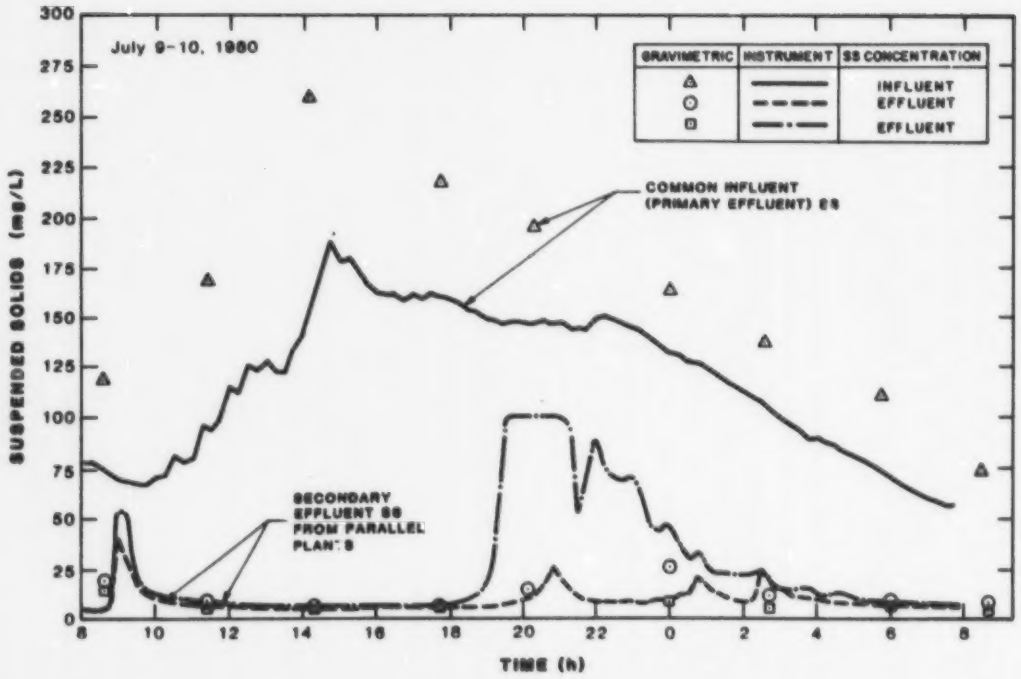

Figure 2. Comparison of instrument response and gravimetric determinations for influent and effluent suspended solids (Stephenson *et al.* 1983).

plants had deteriorated. This was reflected in the response of the effluent SS at the peak overflow rate which occurred between 16:00 and 24:00 hours. The online effluent SS saturated the instrument range at 100 mg SS/L in one of the systems. The other treatment system continued to produce an acceptable effluent. The grab sample data showed relatively good conformance with the online results. The potentially rapid response of suspended solids concentration to operational conditions suggests that online determination is applicable for early detection of process response. Routine maintenance and calibration checks are required to achieve satisfactory ongoing performance.

Figure 3 shows the online measurement of flow, MLSS, and returned activated sludge concentrations in a full-scale activated sludge facility. The return activated sludge concentration, from which the waste activated sludge is derived, responds directly to the feed flow rate and corresponding solids loading to the clarifier. Grab sampling of the return stream for solids retention time control could result in inaccurate calculation of the correct sludge wastage rate.

Dissolved Oxygen

In aerobic wastewater treatment the dissolved oxygen concentration is a necessary measurement to ensure that effective aeration occurs. Inadequate dissolved oxygen concentration can lead to treatment problems such as poor settleability or inhibition of nitrification, while excessive aeration is costly from the energy consumption viewpoint (Sorensen 1979) and can lead to settleability problems because of floc shear. Due to the time-varying nature of the dissolved oxygen concentration, point measurements in space and time do not guarantee that the concentration is continuously maintained within a desirable range.

Figure 4 shows the variations encountered in the dissolved oxygen concentration in a completely-mixed activated sludge system subjected to variations in flow and organic loading. These data were acquired from a continuous online DO monitoring instrument with data logged every 90 seconds. The usual manual sampling of DO, once or twice a day, would not effectively quantify the response shown in Figure 4 to the load fluctuations. Successful automatic control of aeration requires an online measurement of DO. Shock organic or toxic loads can also be observed through online DO measurement. Strict precautions must be maintained to ensure that effective maintenance is provided for all immersed sensors since oil and grease or biofilm growths can accumulate and effect measurements. For im-

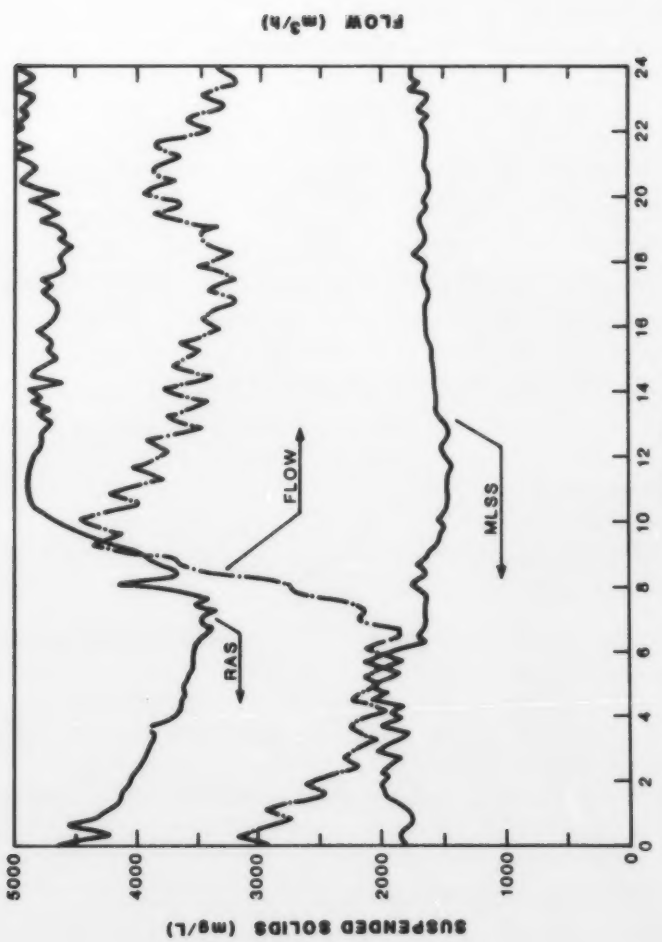

Figure 3. Response of return activated and mixed liquor suspended solids to diurnal variations in plant flow rate.

mersed DO sensors, hydrogen sulphide may poison electrode sensors decreasing the accuracy and sensitivity of the measurement.

Because the loading to most wastewater treatment plants is never at steady state, there are compelling reasons for the industry to adopt continuous online measuring principles to effectively monitor and control the process. Not all measurements are easily automated, e.g. BOD5, and digital microprocessor capabilities should be used effectively to extract the maximum amount of needed information from the readily available measurements (Olsson 1981).

Besides the prerequisite measurements discussed above, other measurements are sometimes necessary in the day-to-day operation of the activated sludge process, e.g. pH. Depending upon the wastewater characteristics and the application, these other measurements may be prerequisite to successful operation.

Advanced Online Analytical (Wet-Chemical) Measurements

In petroleum refinery wastewater treatment systems several other conventional parameters are of interest to maximize the system performance. For example, these parameters include:

- TOC or DOC (dissolved organic carbon)
- NH_3-N
- Phosphorus
- Phenolics
- Biochemical respiration rate
- Oil-in-water

These parameters are of importance from the viewpoint of plant operation and of treated effluent quality. Several commercial online analyzers are available for their measurement. Relatively little field experience is documented for these analyzers. Further, the actual analysis methods may be specific to each manufacturer.

Each manufacturer of analytical equipment provides a unique approach to the chemistry and analytical hardware associated with the analyses. Therefore, each unit must be considered independently from the standpoint of, for example:

- Measurement principle and methodology
- Range
- Accuracy and minimum detection limits
- Reproducibility and drift
- Response time and linearity

This is essential at the predesign stage to ensure that appropriate equipment is available.

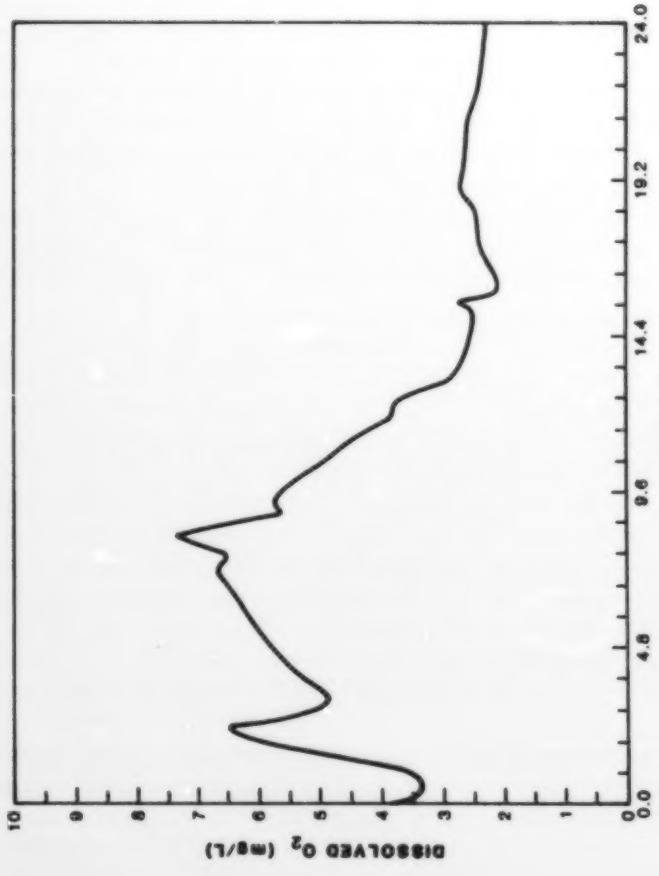

Figure 4. Diurnal response of dissolved oxygen concentration in a completely mixed conventional activated sludge process.

Usage of the above equipment should be considered on a site and application specific basis. Specific usages of the above analytical systems could include:

- Inhibitory spill detection
- Logging alarms and load balancing
- Automatic reporting
- Effluent quality assessment
- Feedback control

For example, detection of an inhibitory plant feed by respiration rate analysis could be used for influent diversion to holding tanks. Similarly, online measurement of sulphides or phenol in raw wastewater could be used for similar diversion techniques followed by subsequent treatment of the diverted wastewater at a controlled rate through the treatment process.

One of the main requirements with these analyzers, as previously discussed, is adequate sample preparation to ensure non-clogging and non-fouling application. This, in conjunction with analyzer maintenance, is crucial to the success of these instruments.

Further, the application of these analyzers downstream of the treatment system could be used as online indicators of process performance. For example, in nitrifying systems, increases in effluent ammonia concentration could warn of impending loss of nitrification. The response of ammonia concentration can be relatively rapid, depending on actual process conditions. The availability of online analysis provides the capability to monitor these types of changes in real time. Figure 5 shows an example of the tracking performance of an online NH_3 analyzer to perturbations in system response. In this example, the online unit corresponded to offline laboratory analyses with a high degree of correlation. Online analyses are shown for a coupled nitrification (NIT)-denitrification (DN) biological fluid bed process.

The successful application of the online wet-chemical instrumentation requires special attention in the design, start-up and routine usage and maintenance phases. This was shown to be crucial, for example, to the usage of an online TOC analyzer (low temperature persulphate ultraviolet oxidation principle) (Stephenson *et al.* 1983). Problems required to be resolved for this unit included:

- Sample preconditioning to minimize tube plugging
- Elimination of reagent crystal blockage of tubing
- Elimination of humidity and condensation in gas tubing to infrared analyzer

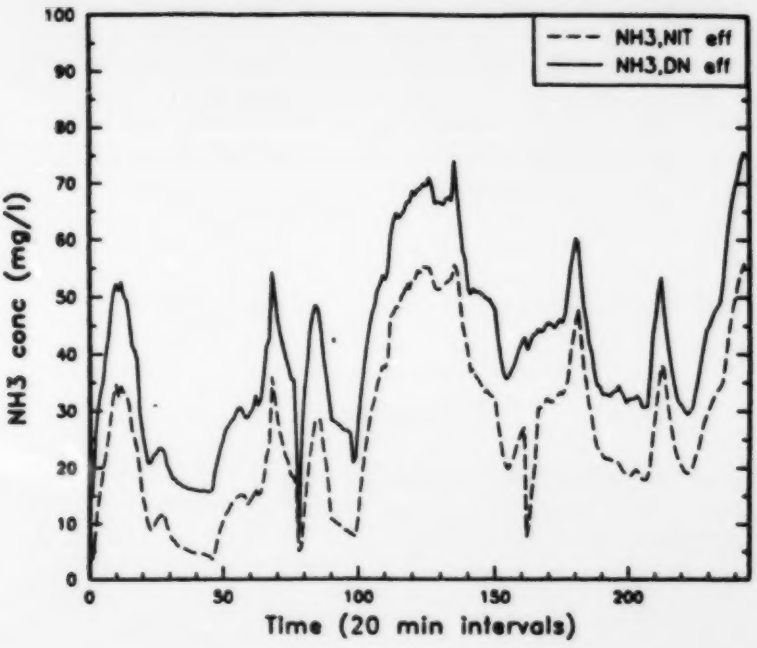

Figure 5. Online NH_3 measurements from nitrifying and denitrifying reactors (Mullin 1986).

- Elimination of UV reactor lamp failures due to insufficient air fan cooling
- Acidification of sampie immediately downstream of the preconditioning step to prevent microbial growth in analyzer tubing and resultant blockages

Even after these corrections, considerable effort (0.5 to 1 day per week) was required for routine calibration and maintenance.

Summary

Online commercially available instrumentation based on process immersion principles or on wet-chemical principles is available for usage in petroleum refinery wastewater treatment facilities. These instruments are capable of assisting with plant operation and performance enhancement. Acceptable performance of the instruments is

highly dependent on proper selection and application, sample preconditioning (for wet-chemical analyzers) and characterization, ongoing maintenance by knowledgeable staff including chemical analysts, and system buy-in with plant staff and supervisors at the predesign and initiation stage. Effective usage of these instruments may lead to improved plant operations with a focus towards trace contaminant control.

Key words: online instrumentation, wastewater treatment

References

Holmstrom, H. and B. Hultman (1981), "Improved Operation of Municipal Wastewater Treatment Plants in Sweden by Use of Instrumentation and Automation". *Water Sci. Technol.* **13(8)**, 7–13.

Knudsen, D.I. (1985), "Wastewater Instrumentation and Control Systems — Management Attention Assures Results". Proceedings of the Seminar Instrumentation and Control Systems in Wastewater Treatment Plants, Burlington, Ontario, March 6.

Manning, A.W. and D.M. Dobs (1979). Design Handbook for Automation of Activated Sludge Wastewater Treatment Plants. U.S. Environmental Protection Service, Contract No. 68-03-2573.

Molvar, A.E. *et al.* (1976). Instrumentation and Automation Experiences in Wastewater Treatment Facilities. Environmental Protection Technology Series, EPA 600/2-76-198.

Mullin, J.F. (1986). Dynamic Operating Characteristics of a Coupled Fluidized Bed Reactor System. M.Eng. Thesis, McMaster University, Hamilton, September.

Olsson, G. (1981). "Control and Automation in Wastewater Treatment — Advances, Unsolved Problems and Challenges". *Water Sci. Technol.* **13(11/12)**, 826–831.

Olsson, G., J. Stephenson and D. Chapman (1986), "Computer Detection of the Impact of Hydraulic Shocks of Plant Performance". *J. WPCF* **58(10)**, 954.

Sorensen, P.E. (1979). Pilot Scale Evaluation of Control Schemes for the Activated Sludge Process. Contributions from the Water Quality Institute, No. 1, 2970 Horsholm, Denmark.

Stephenson, J.P., B.A. Monaghan and L.J. Yust (1983). Pilot Scale Investigation of Computerized Control of the Activated Sludge Process. Report SCAT-12, Environmental Protection Service, Environment Canada, Ottawa.

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Automation of a Petroleum Refinery Wastewater Treatment Plant: A Case Study

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Abstract

Historically, automation was not considered for wastewater treatment plants because it did not significantly affect operating costs, and manual plant operation was considered acceptable. Despite past practices, the BP Oil Refinery at Marcus Hook, Pennsylvania set a new standard when they began upgrading their wastewater facility in 1985. By automating the plant, they ensured safe, reliable operation with minimum labor requirements, process optimization, and long-term reductions in operating costs. Major design features included: a distributed computer control system with monitoring and supervisory capabilities; high-quality control system instruments; control system components; and redundancy and backup to support operation if a component or power failure occurs. In addition, design control philosophies remained consistent from predesign to startup. This advanced wastewater treatment plant can serve as a model for automation of future industrial treatment facilities.

Introduction

Wastewater treatment plants have historically been one of the last areas in an industrial plant to be considered for automation. This situation existed because (1) wastewater treatment plant processes were technically unsophisticated and manual control was adequate and (2) there was little incentive to automate wastewater treatment plants because it did not significantly affect operational costs.

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This situation has changed dramatically in the last decade. The Environmental Protection Agency (EPA) as well as local and state regulatory agencies have adopted more stringent requirements. On a national basis, enforcement of compliance requirements is becoming an important consideration in all industries.

The BP Oil Refinery, located at Marcus Hook, Pennsylvania, is one refinery affected by the changing regulatory climate. In 1985 a decision was made to upgrade the existing wastewater treatment facility to an advanced wastewater treatment plant (AWTP). This is one of the largest privately financed constructions of a wastewater facility by a refinery in the United States (ENR 1988).

An important issue during the predesign phase of the project was the appropriate level of automation for the AWTP. Optimum operation of the more sophisticated processes selected was achievable through automated process control. It was determined that automated control of the AWTP can reduce long-term operating costs in the same way that cost reductions have been realized through automating other areas of the refinery.

This paper discusses the level of automation selected for the BP AWTP at Marcus Hook. The advantages, risks, and potential benefits of the level of automation selected are also discussed. The criteria used for selection of a computer control system are outlined. An overview of the wastewater treatment plant design is included. Finally, as an example, a description of automated control of the primary filter system is provided.

Project Background

The BP Oil Refinery is a 170,000-barrel-per-stream-day petroleum refinery located in southeastern Pennsylvania. The refinery was originally established in the early 1900s on 17 acres of land. Over the years, it has undergone a number of expansions and modernizations, and has changed hands several times. Today, it occupies approximately 350 acres and includes the following major refining processes: crude desalting, atmospheric and vacuum crude distillation, fluid catalytic cracking, alkylation, hydrocracking, hydroprocessing, catalytic reforming, caustic treating, merox treating, and hydro treating. Some major products are motor gasoline, jet fuel, diesel fuel, home heating oil, residual fuel, and liquid petroleum gas.

The refinery is classified by the EPA as a subcategory B ("cracking") refinery. Wastewater, at an average rate of 5.7 mgd, is discharged through three permitted outfalls to the Delaware River by way of Marcus Hook and Stony Creeks.

In 1985, BP Oil commissioned a design for wastewater treatment plant improvements. The project's objective was to revamp the wastewater treatment facilities and to provide additional treatment processes as required.

A block diagram of the existing AWTP and improvements is shown in Figure 1. The design of the plant is typical of advanced wastewater treatment plants in refineries except that the primary upflow filters follow the American Petroleum Institute (API) separators. Typically, a dissolved air flotation unit would be used in this location. The filters were selected following pilot studies in which performance was compared to downflow filter systems (Davis and Irani 1988). The impact of these filters on the control system is discussed in the "Primary Filter Control" section.

The design phase of the project began in 1985 and construction started in 1987. The plant was started up in spring 1989.

Control System Design Approach

Level of Automation

The primary objective in determining the level of automation in the AWTP was to provide a control system capable of reliably operating the plant with minimum labor requirements. Personnel from the refinery and from the engineering firm providing control system design worked together to determine the best way to meet this objective. The control system selected includes (1) a distributed computer control system, (2) a central control room for monitoring and remote control, and (3) local control panels for process startup and maintenance.

Operating Philosophy

The design objective was to provide a control system that allowed maximum automatic unattended plant operation. It was decided that labor-intensive processes would be automated through the computer control system. These processes consist of the primary filter system and associated backwash sequences, the activated sludge system, the dissolved air flotation (DAF) thickening unit, the tertiary filter system, and the plate and frame filter press chemical and feed sequences. The successful implementation of automated control in these areas would significantly reduce the number of operators required to monitor and supervise the processes. In addition, the

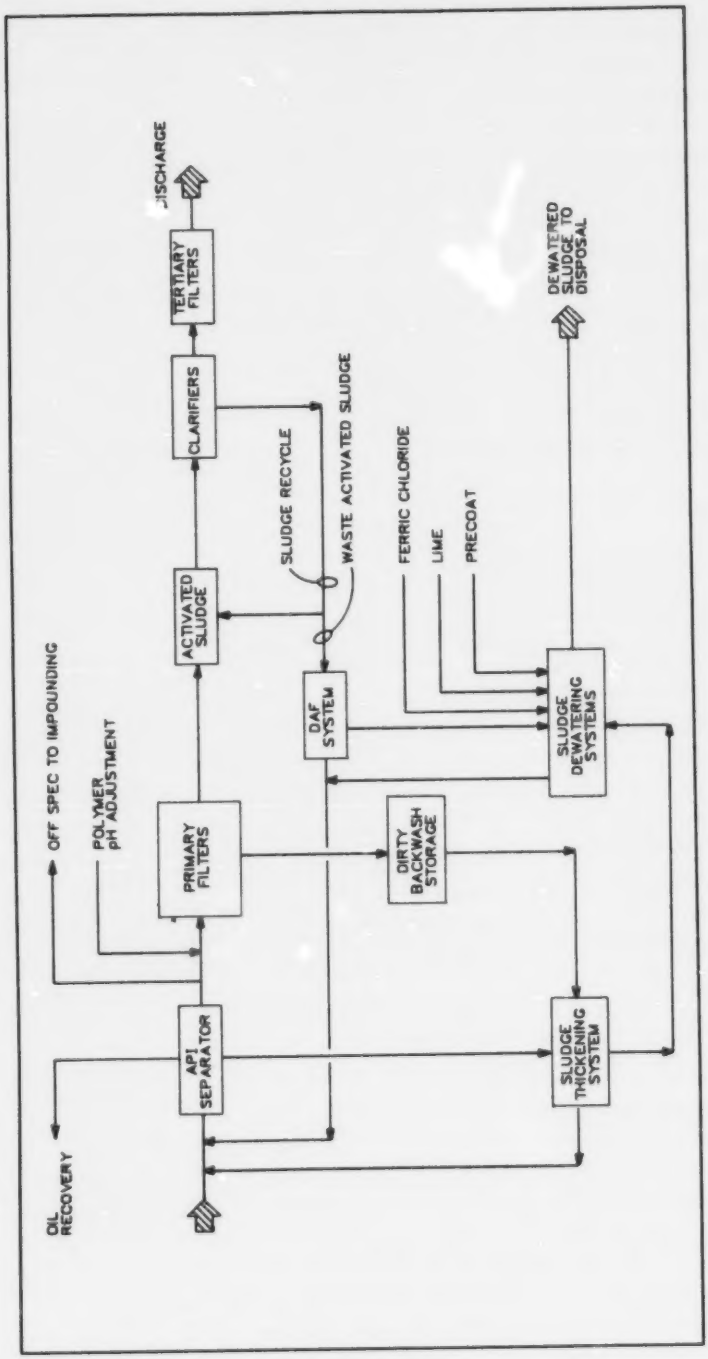

Figure 1. Plant flow block diagram.

control system would be required to meet regulatory guidelines under all operating conditions.

Sequences are designed to be operator initiated or automatically initiated based on operating conditions. Once started, they operate unattended unless an abnormal operating condition arises. When this occurs, an alarm generated by the computer control system notifies the operators.

The following guidelines were used to set up alarm standards:

- Each analog signal is monitored and an alarm issued for loss of signal or signals out of range.
- Each pump, valve, or other equipment controlled through the computer control system is monitored for failure.
- Each step of automated sequences is monitored for failure.
- Each control system component is monitored for failure.

This approach to alarm generation results in an increased number of alarms when compared to a manually controlled process. These alarms are required to ensure safe and reliable plant operation. In many situations, supervision and monitoring by the control system replaced direct operator supervision. The alarms ensure that abnormal conditions are brought to the attention of the operating personnel.

Quality Assurance

Unreliable operation of automated control systems frequently can be attributed to poor performance of primary elements, valves, and other field devices. To alleviate this problem, quality was an important consideration in selection of valves, flow meters, sensors, and all other devices that interface to the control system. Instruments used in similar installations that had performed reliably were selected. In many instances, the initial cost of these instruments was greater than alternative selections. However, reliability, long-term maintenance, and replacement costs were the significant criteria used in the selection process.

Failure Analysis

Operation of the AWTP in the event of power failure or transients was addressed during control system design. Because the computer control system is integral to plant operation, the design ensured reliability.

There are power supplies from two different sources feeding the plant. If both power supplies were cut off, two jet engine-powered

generators would support the operation of selected pumps. The API separator effluent would be routed by gravity flow to a large impounding pond where it would be stored for future treatment.

Under normal operating conditions, power supplied to the control system components is conditioned, and critical components have limited battery backup so transient power surges will not affect performance.

Design Consistency

An important factor in ensuring successful control system implementation was consistency of approach throughout the project. The control system philosophies developed during the predesign phase were defined in greater detail but not significantly modified during the project.

In computer-controlled system implementation, problems often occur when design philosophies are revised as the project progresses. This is true of computer control systems because the computer provides flexibility. For example, if the overall control philosophy is modified on a unit-by-unit basis, the operators can be confused by the inconsistent approach and operating procedures that result. In this project, a consistent approach to control was maintained from predesign through startup. In addition, the control system design personnel were experienced in the control of AWTP facilities. These personnel followed the project from design through startup. The question of redundancy was also addressed during control system design. A description of the approach taken follows the discussion of control system selection.

Control System Selection

A decision was made during predesign to install a distributed control system (DCS). This system was defined as follows:

- Control capabilities reside in more than one computer control system module
- Control system components are "intelligent" because they are digital and can be programmed
- The control system components "communicate" with each other sharing information

An advantage of the DCS architecture is the reduction of risk should a single control system component fail.

A study was done to evaluate available control systems and to select a system that best met the requirements for the AWTP. Selection factors included:

- Plant operating philosophy
- Number and location of operator interface (CRT) units
- Availability of maintenance and local support
- Ease of upgrade and expansion
- Reputation of supplier

The architecture of the control system selected used programmable logic controllers (PLCs) as local control units and a microcomputer as the supervisory unit. The suppliers of the programmable controllers and the microcomputer have a history of successfully providing computer control systems.

The PLCs will perform all continuous and sequential control of the processes. The supervisory computer provides the following functions:

- Supervisory control over the PLCs
- Interactive color graphic process displays
- Alarm handling routines
- Real-time data trending
- Shift, daily, and laboratory reports
- Historical data collection and retrieval

A block diagram of the configuration of the selected control system is shown in Figure 2.

Distributed Units

Three PLCs are used to provide local control in the following configuration: (1) the primary filter system, (2) the tertiary filter system, and (3) the remainder of the plant. By providing control through more than one component, the risk of failure of any single unit is minimized. The control system software has been developed so that each PLC can function independently of the other PLCs and of the supervisory computer. This design philosophy limits the effect of failure of any single control system component.

Standardization of Control System Components

Programmable logic controllers were selected for this project in part because of vendor requirements. The vendors providing the two

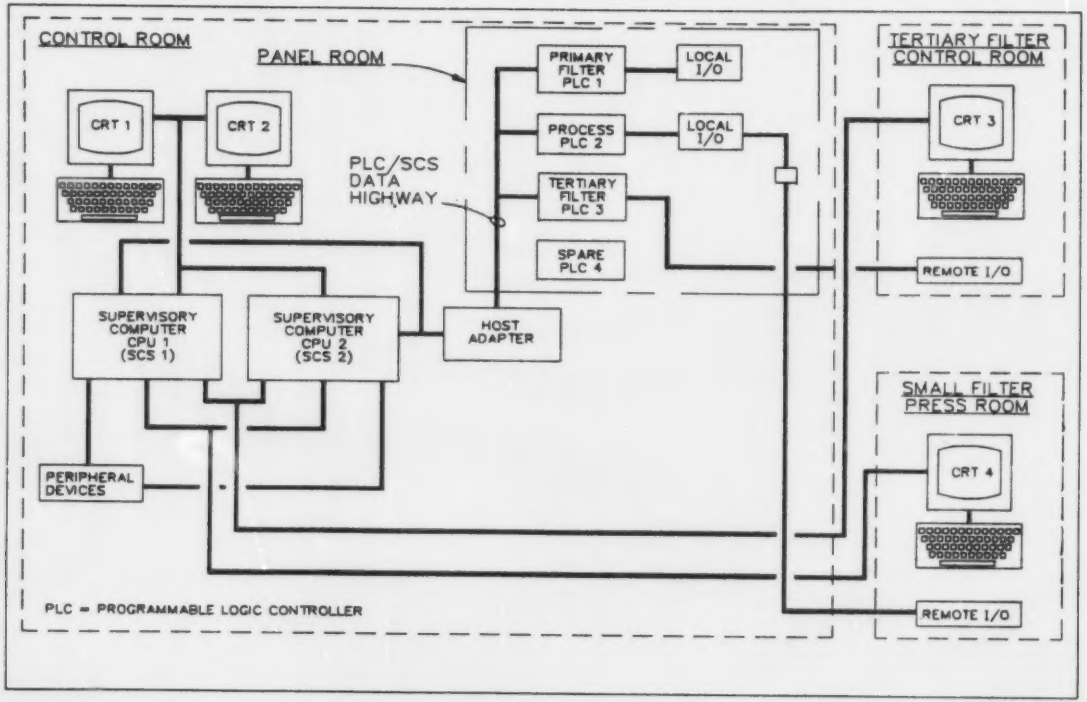

Figure 2. Computer control system block diagram.

filter systems, the primary and tertiary filter systems, normally provide PLCs as part of their package systems. In this instance, a single PLC supplier was selected and the vendors modified their packages to include the selected PLC. This standardization ensured that the three PLCs provided were identical, leading to lower maintenance costs and easier training of personnel.

Redundancy

Redundancy was accomplished on this project through several different philosophies. It depended on the importance, cost, and feasibility of providing backup units for the control system components. The supervisory computer system (SCS) is a redundant unit that automatically switches to the backup unit when a failure is detected. If both units fail, the PLCs would continue to operate based on the last set points received from the supervisory computer. There are also panel-mounted devices for limited monitoring of PLC operation.

A fully dedicated spare PLC is installed in the same rack with the three operating PLCs. If one of the PLCs fails, the program for the failed PLC can be loaded into the spare PLC and brought online in 10 to 30 minutes. The equipment affected by a failed PLC can be manually controlled from the local control panels while the spare PLC is brought online. PLCs are reliable field hardened units, frequently operating for years without failure. This approach to providing backup is a cost-effective approach when the anticipated need for a spare is relatively low.

Primary Filter Control

During early project design, the performance of coalescing filters and DAF systems for fine oil removal were compared. The comparison showed that filters would provide better effluent quality more consistently, require less space for installation, and would not need future retrofitting for air pollution control. Initial capital cost for the filter system was greater than the initial cost of the DAF system; however, the higher energy and polymer consumptions of the DAF system would offset this advantage during the life of the project. On the basis of the above facts, the decision was made to install filters for fine oil removal downstream of the API separators and upstream of biological treatment. Automated control of the filter operation and required backwash sequences provided the opportunity to minimize labor costs.

The design called for installation of five 15-foot coalesce-type, upflow filters. The filters use API separator effluent wastewater for the backwash cycles. The pilot study indicated that backwash sequence duration would average 50 to 55 minutes, with an average of four backwashes required per filter per day (Davis and Irani 1988). The backwash sequence is a 37-step automated procedure.

Figure 3 shows a display of a single filter with associated valving and equipment. These diagrams are black and white copies of color graphic displays provided to the operators for monitoring and control at the operator CRT units.

The automated filter operation and backwash sequences reside in the PLCs. The backwash sequences are initiated by operators at the CRT graphic displays or automatically, depending on high pressure drop across a filter. Once started, the backwash sequence proceeds through the steps opening and closing valves and starting and stopping equipment as required. Backwash messages, indicating the current step and activity during the operation, are displayed at the operator CRT unit. The backwash sequence progresses without operator attention. If a step is not successfully completed for any reason, such as a valve not opening when requested to, the sequence goes to "hold" status and an alarm is issued.

The labor saving resulting from automated control of the primary filters is readily seen. If an average of twenty 50-minute manual backwashes are performed daily, an operator would be required around-the-clock to supervise the backwashes.

In addition, there are numerous restrictions and interlocks related to the primary filter operation and backwash sequences. Some requirements are listed below:

- Inhibit backwash if the selected backwash tank volume is below the requirement to complete the backwash.
- Limit the number of filters in backwash to two at any one time.
- Establish minimum and maximum flow rates for a single filter.
- If the dirty backwash tank is too full, initiate backwash "hold" when a filter backwash reaches the associated steps.

The complexity of the backwash sequences and associated interlocks means that manual operation of the primary filter systems would be extremely difficult to implement, and would demand a high degree of operator training. Therefore, automation of these systems will simplify operation and guarantee consistent, optimum control.

The primary filter control is only one example of automated control in this AWTP. A similar approach was taken with all unit

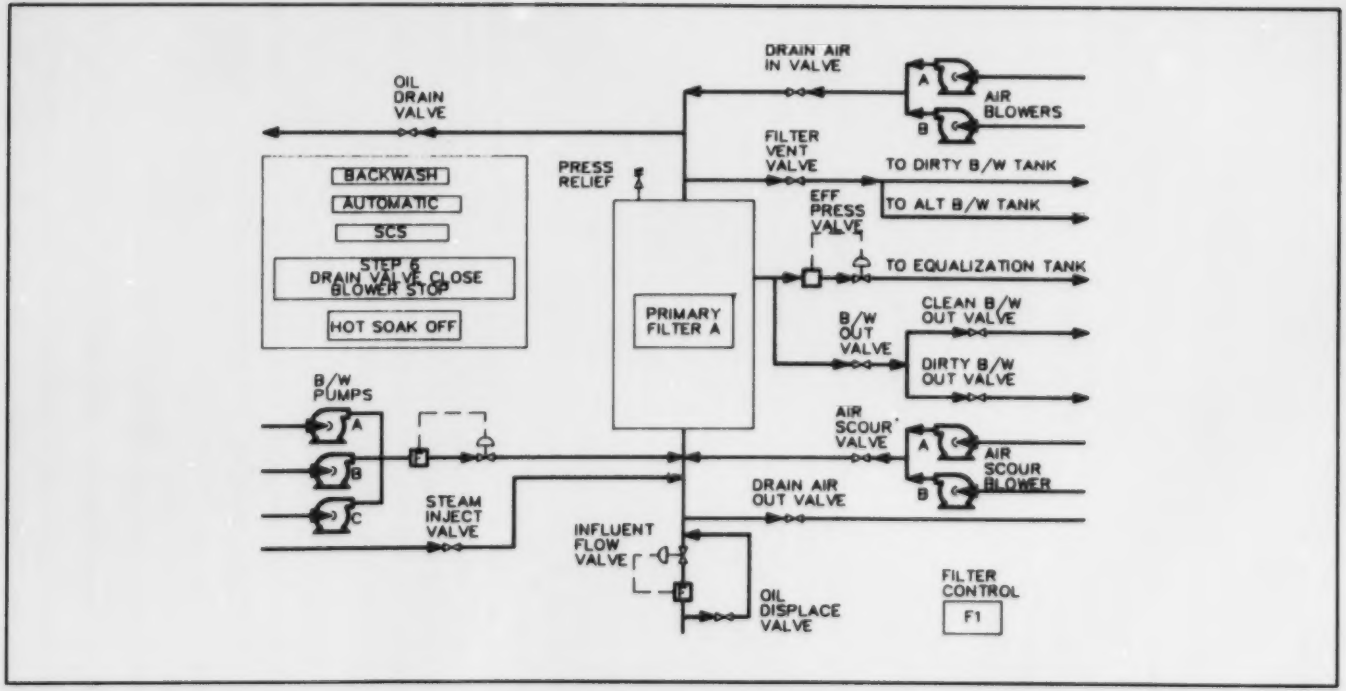

Figure 3. Primary filter A — detail display.

processes throughout the plant in order to minimize long-term labor requirements.

Performance Evaluation

The BP AWTP has been in operation for several months. To date, it has fulfilled all regulatory requirements while performing efficiently. The control system has been able to automatically handle varying influent conditions. It has managed drops in influent pH, increases in influent flow after rainstorms, and periodic increases in organic loading without the need for operator intervention.

Conclusion

Automation of wastewater treatment plants in a refinery provides an opportunity to realize a long-term reduction in operation costs. Steps can be taken throughout the project to ensure that the control system implementation is successful. These steps are outlined below.

The level of automation and the operating philosophy should be defined early in the design phase. Failure analysis during design, quality assurance when selecting control system components, experienced control system designers, and design consistency throughout the project can all contribute to the project's success.

Selection of the computer control system should satisfy criteria established to meet plant requirements. Standardization of control system components provided with vendor-supplied equipment can simplify training and maintenance requirements. Finally, control system architecture and the level of redundancy are important issues to be addressed during design.

Key words: Petroleum refinery wastewater system. Automation. Potential benefits; reliability, cost reduction. Risks.

References

Anonymous. January 14, 1988. News. ENR. McGraw-Hill, Inc. New York. Pp. 6–7.

Davis, M. and M. Irani (1988), "API separator filtration pilot filter study". *Hydrocarbon Processing Symposium Proceedings*, New Orleans. PD-Vol. 13, 17–38.

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Optimization and Control Petroleum Refinery Wastewater Treatment Systems — Status, Trends and Needs

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Abstract

Based on discussions in workshop sessions, several recurring themes became evident with respect to the optimization and control of petroleum refinery wastewater treatment systems to achieve effective removal of toxic contaminants. It was apparent that statistical process control (SPC) techniques are finding more widespread use and have been found to be effective. However, the implementation of real-time process control strategies in petroleum refinery wastewater treatment systems is in its infancy. Considerable effort will need to be expended to demonstrate the practicality of on-line sensors and the utility of automated process control in petroleum refinery wastewater treatment systems. This paper provides a summary of the discussions held at the workshop.

Introduction

As part of the workshop on "Optimization and Control of Petroleum Refinery Wastewater Treatment Systems", parallel sessions were conducted on each of the six plenary subject areas. Facilitators and assistants were responsible for directing and maintaining relevant discussion and for the recording of these discussions for subsequent summation by the session presenters. The objectives of the sessions were:

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- to define the present status of the petroleum refinery industry in achieving the goal of effective control of toxic contaminants and toxicity;
- to determine areas where improvements are needed in the industry to meet future regulations in the area of toxics and toxicity control; and
- to identify priority areas of research and development required to achieve the goals and future requirements.

Presented herein are brief summaries of the discussions and conclusions from each of the workshop sessions.

Design and Operation of Refinery Treatment Systems for Toxic Contaminant Control

Present Status

The design of wastewater treatment facilities in the industry is fairly consistent, normally incorporating some form of pretreatment (API separators, flotation, filtration) prior to biological treatment and, in many cases, effluent polishing by unit processes such as filtration. In situations where upgrading of effluent quality was mandated, a few facilities had incorporated powdered activated carbon (PAC) addition. Fewer had implemented any sophisticated level of tertiary treatment by unit processes such as granular activated carbon (GAC) adsorption or chemical oxidation (ozonation).

The most important single process from the standpoint of toxics and toxicity control was considered to be the activated sludge system. Solids Retention Time (SRT) was acknowledged to be a critical operating parameter but one which many facilities did not rigidly control. Operation at long SRTs has been shown to reduce the PAC requirements in PACT processes and allow nitrification which contributes to reduced effluent toxicity.

Manual control of process operations is virtually universal, with the exception of DO control which is automated in a very few refineries. Statistical process control (SPC) procedures have recently been implemented at some facilities, focusing on final effluent quality and raw wastewater quality. These procedures have generally been demonstrated to reduce the variability of both the treated effluent stream and the process wastewater. SPC data analyses have been limited to conventional parameters such as TOC, COD, Total Phenols and Oil & Grease.

Although the biological process was held to be the key to effective toxics control, source control and pretreatment were identified as critical to efficient biological treatment plant operation. A well-designed treatment plant will not provide effective control in the absence of a facility-wide commitment to minimizing process area spills and discharges that would impair the system operation. In this regard, the application of SPC procedures to process wastewater quality data can be as valuable as their application to the final effluent data.

Problem Areas

In terms of biological process performance, consistently achieving nitrification to meet effluent ammonia requirements represents a challenge at most refineries. Meeting effluent limits on phenol in the 10 ug/L range on a consistent basis is also difficult.

The lack of a defined correlation between effluent quality, as measured analytically, and effluent toxicity represents a problem from the standpoint of process control and system operation. Effective use of traditional sampling, analysis and data management techniques may not ensure compliance with effluent toxicity limits, particularly when the specific cause of the toxic response is unknown or is intermittent.

The traditional view of the wastewater treatment plant as being less important than production units needs to be changed. The lack of continuity resulting from operator staff and technical support staff rotations was an example cited of management approaches which hindered efficient and effective treatment plant operation. Source control needs to be emphasized from upper management through to production and maintenance staff. Specifications on acceptable process wastewater quality need to be developed similar to existing specifications for feed streams to other unit processes.

The lack of a comprehensive database that incorporates refinery effluent toxicity results with refinery design (unit processes, crude types, etc.), water management practices, wastewater treatment plant design, operation and performance, and chemical (conventional and trace) characteristics hinders effective problem solving.

Future Needs

The present approach to petroleum refinery treatment system design has proven to be effective. In meeting more stringent effluent quality requirements that incorporate toxic contaminant and toxicity limits, emphasis should be placed on source control. Innovative approaches are needed, including developing and maintaining

process wastewater specifications, implementing a permit system for discharges from individual process units or developing an allotment schedule (kg/day based) for discharges from process units. SPC techniques applied to process wastewater quality at the treatment plant can successfully reduce the variability of the wastewater stream.

The addition of sophisticated tertiary treatment processes such as GAC adsorption does not appear to represent a remedy for the problem at all refineries. More stringent SRT control, either by manual or automatic means, would improve process performance in many cases and should be the essential first step in optimizing an existing system. The end-of-pipe treatment process and the refinery operation both need to be considered. In many cases, there are insufficient data available to identify a cost-effective solution to the toxics and toxicity problems.

The development of an industry-wide database of toxicity and toxic contaminant results would be beneficial from the standpoint of identifying the magnitude of the problem and focusing the development of appropriate solutions.

Management and Analysis of Data from Petroleum Refinery Wastewater Treatment Plants

Present Status

a) Data Sources: Four types of data are collected by petroleum refinery wastewater treatment plants: regulatory data, supplementary effluent data, process monitoring data, and data concerning the quality of feed into the wastewater treatment plant. Regulatory data is collected at a frequency and reported in a manner dictated by the various regulatory authorities. In the United States, regulatory requirements vary on a state-by-state basis. Currently, the American Petroleum Institute is compiling a database on permit requirements for all refineries in the United States (Laffly, 1989). To complete the picture regarding the overall performance of the wastewater treatment plant, many refineries conduct supplemental effluent sampling.

Daily monitoring of the various unit processes is conducted to control the operation of the plant. Because timeliness is of the essence, process data should be collected using installed or portable instruments or simplified field test kits. The quality of feed streams into the plant is often monitored to prevent dumps of toxic material and improve source control. Some plants are equipped with swing-tanks which receive the discharge from a unit process in the refinery.

The liquid in these tanks is only discharged for treatment after it has been checked to ensure that it will not adversely affect the treatment process.

There is a wide range of practices being used at refineries in terms of how to sample, where to sample, and how to manage and analyze the data. The majority of the refineries are currently handling data on a manual basis. Impending legislation in Canada and the United States will vastly increase the quantity of data generated, making the use of an automated data management system essential.

b) Database Management Software: There are three options for obtaining database management software. Firstly, the refinery can have its staff create the necessary program from scratch using languages such as FORTRAN, BASIC, C, etc. Alternatively, a programmable database management package such as dBase can be purchased and employed to design the necessary data input and reporting forms. dBase IV is the most recent version in the dBase line. A third alternative is to purchase a program which has been tailored by a consultant or vendor to the needs of the refinery.

As most technical personnel are familiar with them, spreadsheet packages such as Lotus 1-2-3 deserve consideration for the management and analysis of small databases. Lotus 1-2-3 can handle up to approximately 800 data records (Gabaldon, 1988). However, it does not have the advanced capabilities of a true database management package. Inexpensive add-on packages are available for spreadsheet packages to improve both database management and statistical analysis capabilities (Gabaldon, 1988; PC Magazine, 1989). The development of macros for constructing quality control charts and performing simple linear regression is discussed by Cheremisinoff (1988).

Factors important in selecting the most appropriate alternative include the technical and financial resources available to the refinery, the size and nature of the database, the amount of time required to complete the conversion and how the data is to be used. Software must be maintained and updated over time. Whatever approach is adopted, it is essential that the use of a computerized database management system be phased in realistically.

c) Case Study: A computerized database management system has been implemented at two Chevron refineries in California. Quality control techniques were initiated approximately 18 months ago following a decision by senior management. Data management and analysis software was programmed in-house and all staff (managers included) were provided training in statistical process control. At the wastewater treatment plant, quality control charts are constructed

for both influent (feed quality) and effluent data. Feed quality control ensures that waste management practices in the refinery process units are being rigidly followed, an essential factor in efficient treatment plant operation. Meetings are held on a regular basis to review the results. Values contained in the database are cross-referenced to operators' comments concerning process conditions. Both the level and variability of the effluent from the treatment plants have improved since the implementation of statistical process control techniques.

Future goals in improving data management and analysis at the Chevron refinery treatment plants include encouraging plant staff to make better use of the data. This will involve addressing questions such as: what will happen if the current trend displayed in the data continues? The success of the system has increased the demand on the research and development group to provide technical support to the operations staff. Having detected a problem, additional work is required to develop solutions. Interest is growing in the area of multivariate data analysis to enable relationships to be established between a variety of parameters. One frustration continues: despite improved performance in the removal of a variety of chemical constituents — effluent toxicity remains difficult to control.

Future Needs

Steps should be taken to improve the management of all types of data collected at petroleum refinery wastewater treatment plants. This should include the joint development or selection of software by the petroleum refining industry. A joint approach would enable databases with a common structure and format to be generated.

Secondly, there should be joint action by industry to address the issue of handling and analyzing trace contaminant data containing 'not detected' results ('non-detects'), particularly when estimating mass loadings of trace contaminants. Since mass loadings are estimated as the product of flows and concentrations, assumptions regarding 'non-detects' can have a profound effect on the estimates. If all of the values of a particular substance were reported as 'non-detect' and a value of the method detection limit used in mass loading calculations, substantial loadings could result when in fact there is no evidence that the substance is present in the effluent.

It was also emphasized that data collection alone does not result in improvements in process performance. The data collection program must be tailored to an plant control strategy, either manually or automatically implemented. The data management program must provide information to the plant operations staff to allow effective decision-making.

Chemical Monitoring: Effective Use of Chemical Analysis for Optimization of Contaminant Removal

Present Status

Properly designed and operated treatment systems provide effective, efficient trace contaminant control. At present, extensive and expensive trace contaminant monitoring programs are being undertaken in Canada and the United States to demonstrate that a high level of performance is being achieved. A well established short-list of specific contaminants has been identified for monitoring purpose including benzene, toluene, xylene, ethylbenzene and phenol as well as others.

No surrogate parameter has been statistically identified as an indicator of toxics removal. Phenol or total phenolics is most commonly monitored with this intent, but the low level concentrations of most toxic trace contaminants makes establishing a surrogate extremely difficult. There has been no rigorous attempt to utilize trace contaminant monitoring data for wastewater treatment process optimization. Conventional contaminant data would appear to be more suitable for this purpose because of the higher variability in trace contaminant data, the frequency of 'non-detects' results and the expense associated with these analyses. Lack of confidence in the accuracy of trace contaminant data was also perceived to be a limiting factor in the application of these data for process control purposes.

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Problem Areas

Concerns were raised with respect to the present level of understanding of the basic principles of treatment plant operation and the ability to accurately predict even conventional contaminant removal performance. Presently, data are insufficient to enable a correlation to be established between toxics removal performance and process operation. Historically, studies in the United States and Canada have shown non-detectable levels of most trace organic contaminants in petroleum refinery effluents. Furthermore, the full potential of the

treatment plant to achieve toxics removal and toxicity control has not been established.

The lack of statistical correlation between the results of toxicity tests and chemical analyses of wastewater treatment plant effluents presents a serious obstacle to effective process optimization and process control. This problem is compounded by the relatively high variability of the chemical analysis data at near detection limit concentrations. This analytical variability has significant implications in determining the state of compliance of a discharge with a regulatory limit.

A consistent data management approach is needed to eliminate the present random approach to the handling of issues such as including non-detected concentrations in averages and loading calculations. This standardized data management would also alleviate public perception problems related to data reported in different manners from different sources (ie. 0.001 ppm vs. 1.0 ppb vs. 1000 ppt).

Future Needs

A joint industry effort is needed to formalize a consistent, rigorous data management system. This system should allow a level of data analysis and interpretation rather than simply providing a regulatory reporting function.

Additional research is needed to provide further insight into the mechanisms of toxic contaminant and toxicity removal in existing treatment facilities. This effort should address, as an objective, defining the full potential of these treatment systems to effect toxics and toxicity removal. This research effort should also consider the development of biodegradation data on specific organic compounds. Such data would be useful from the standpoint of selection of chemicals for use in production areas based on the potential impact on the wastewater treatment facility and effluent toxicity.

A review of analytical variability, for both conventional and trace contaminants, would be timely. Significant improvements have been made in analytical procedures and hardware. At the same time, regulatory agencies are specifying extremely low detection limits for specific compounds. Effluent regulations are being set at near detection limit levels without due consideration for the impact of analytical variability on compliance status.

Toxicity Measurement and Reduction Procedures

Present Status

Support is growing for the use of biological testing as an adjunct to traditional chemical analysis of effluent quality. If the goal of wastewater treatment is protection of the ecosystem and the receiving water biota, then biological testing is the most appropriate measure of the ability of the treatment system to achieve that goal. Biomonitoring test procedures and the permitted limits on effluent toxicity should be formulated with due consideration for the condition and use of the receiving stream. Mixing zones also need to be considered in the application of toxicity limits for specific sites.

Results from toxicity tests often appear to be more variable than those from analytical chemistry tests. Much of the apparent variability may result from less rigid procedures and less rigorous QA/QC protocols in biological testing compared to analytical chemistry. The variability in toxicity test results conducted by reputable testing laboratories is similar to that observed in trace organic analyses.

The Toxicity Reduction Evaluation (TRE) procedures developed by the U.S. EPA to identify causative agents of toxicity in effluents and develop methods to reduce effluent toxicity had been used with some variation at several refineries. The degree of success reported among those refineries that had applied Toxicity Reduction Evaluation (TRE) programmes was mixed. Many were successful in isolating the cause of toxicity in their effluents and eliminated the problem by substitution of alternate chemicals or by process modifications. Others were unsuccessful despite large expenditures on TREs. In several cases, the toxicant was identified without application of the detailed TRE fractionation procedures.

Problems

The major concern associated with the application of toxicity-based limits on effluent discharges was the lack of correlation between biomonitoring test results and conventional indicators of treatment plant performance. Intrinsic to this concern is the perceived variability of test results (toxicity tests and analytical measurements), the diversity of test protocols and the non-quantitative interpretation of the test results.

TREs, although useful tools in concept, were considered to be expensive in many situations. It was also felt that the application of these procedures should not necessarily be based on a rigid, mandated protocol since refinery personnel in many instances are aware of the likely contributors to effluent toxicity.

Future Needs

Since biomonitoring and toxicity limits will be components of regulations in both Canada and the United States, it was concluded that the industry must take a proactive role in the development of the legislation. This approach will assist in establishing achievable limits, defining test protocols and heightening public awareness of the issues. To support this proactive participation, industry should encourage and support research aimed at the following objectives:

- Standardization of biomonitoring test procedures and QA/QC protocols.
- Establishment of boundary conditions and acceptable limits on effluent discharges (ie. zero effect vs. discharge with acceptable impact).

Further emphasis should also be placed on establishing the relationship between biomonitoring results and the results of traditional chemical analysis of effluent quality. Optimization of existing facilities to meet effluent toxicity limits will be extremely difficult without a more fundamental understanding of the causes of toxicity in the effluent, the sources of the causal agents in the refinery and their fate in the wastewater treatment process.

On-Line Instrumentation of Petroleum Refinery Wastewater Treatment Plants

Present Status

At present, the extent of application of on-line instrumentation in petroleum refinery wastewater treatment facilities is very limited. Instrumentation for flow monitoring instrumentation, level measurement, pH and temperature is in widespread use. Dissolved oxygen (DO) sensors have found less widespread application. The experience with this instrumentation has been mixed. Flow measurement equipment, which has been based on open channel and closed pipe devices, has generally performed well. However, accurate calibration of the primary sensor at high flow rates represents a problem, particularly with closed pipe devices. Immersion probes for measurement of pH, temperature and DO have been found to be susceptible to fouling, by oil and biological growth. High velocity or sample conditioning is essential for successful operation of such equipment. In most cases, too little attention is paid to these components of the

system. Self-cleaning features on immersion probes may also be desirable. Unfortunately, few manufacturers offer such features.

The present state-of-the-art of on-line instrumentation is not adequate. Significant improvements in the operating and maintenance characteristics of this equipment are needed before they can be considered to be cost-effective. Application of instrumentation should be selective. The focus should be placed on the measurement of parameters for which an operator response is possible, rather than on data logging functions.

Many refineries have successfully used non-standard 'quickie' off-line wet chemical tests to establish influent characteristics or process performance for operational control purposes. These tests can be done on a frequent basis (several times per shift if necessary) and are relatively inexpensive. An inventory of commercially available test kits would assist the industry in selection of appropriate, reliable chemistry for this type of monitoring.

The importance of source control and pretreatment, as identified in the section on design and operation, was reiterated. Emphasis of on-line monitoring should be placed on the process wastewater influent to the treatment facility rather than effluent monitoring. These data would allow positive operator response to changing influent conditions. Conversely, effluent monitoring generally provides data too late to allow positive action to be taken by operational staff. Influent monitoring represents the most severe application of on-line instrumentation. Emphasis must be placed on sample pretreatment in such applications to reduce fouling problems.

Because of the severe operating conditions to which the equipment is exposed, careful selection of parameters for continuous monitoring is important. A load-type measurement, such as total organic carbon (TOC) or total oxygen demand (TOD), has been used with some success in monitoring influent characteristics as part of source control programmes.

Future Needs

The key parameters for which continuous monitoring data would be beneficial include:

- influent load (TOC or TOD),
- effluent suspended solids,
- pH,
- dissolved oxygen concentration in aeration tanks,
- oil content, and
- bioactivity (respiration rate).

Additional emphasis needs to be placed on the site-specific installation design details of this instrumentation. Sample conditioning, along with management commitment to the value of any on-line data, is critical to the success of the on-line monitoring program.

Other priority development needs which would improve the acceptability of on-line instrumentation in the industry include:

- Demonstration of long-term successful operation of appropriately selected and installed equipment.
- Development of a better understanding of the benefits associated with on-line measurement of selective critical parameters through demonstration of improved treatment performance and/or reduced treatment cost.

Participation in an organization such as the Instrumentation Testing Association, with the objective of improving the operational characteristics of available instrumentation, is a worthwhile goal.

Optimizing Process Control in a Refinery Wastewater Treatment System

Present Status

Historically, implementation of on-line process control strategies in refinery treatment plants has not been perceived to be cost-effective since labour savings were seldom realized and energy savings were not significant. The limited use of on-line sensors in the industry demonstrates the lack of confidence in the available technology. Furthermore, there has been little attempt to develop 'cause-effect' relationships in the treatment processes that are essential for the implementation of effective control strategies.

The level of sophistication of existing manual control strategies in many facilities is rudimentary. SRT control is not widely practiced. Despite this, the treatment facilities have generally performed well. Therefore, management has not seen treatment plant optimization through sophisticated process control as a high priority.

Treatment plant automation, as described in the plenary paper, has increasingly been implemented as a labour-saving approach in treatment plants recently with the development of Programmable Logic Controller and Personal Computer (PLC/PC) based distributed control systems. It is important to differentiate between 'automation' and 'process control' in these applications. Automation refers to the sequential implementation of specific functions in

response to a timer-activated or measured signal. Process control, on the other hand, implies the adjustment of an operating parameter (independent variable) to maintain or adjust a dependent variable based on a known causal relationship.

Future Trends

Increasingly stringent effluent quality requirements will force improved performance of existing treatment facilities or large capital expenditures to upgrade existing systems. Process optimization may represent, in these circumstances, a cost-effective alternative to maintain compliance without major expenditures. On-line process control may reduce the variability presently experienced in manually-controlled facilities, reducing the risk of non-compliance.

The implementation of on-line control strategies will require education of operational staff and upper management. A greater degree of confidence in the performance of on-line instrumentation in the treatment plant environment is essential. Benefits, both in reduced costs and improved performance, will need to be demonstrated. The acceptance of instrumentation and control (I&C) procedures in treatment plants in the petroleum refining industry may require a phased implementation approach involving initial on-line monitoring of key performance indicators without control actions (open-loop), followed by a phase-in of closed-loop control after the instrumentation is proven and 'cause-effect' relationships are established.

Future Needs

Acceptance of the utility of on-line process control in refinery wastewater treatment plants will require a demonstration of its benefits, in terms of both improved performance and cost-effectiveness. Operations staff and management need to be committed to the success of the project. This may require a phased implementation approach to develop confidence and experience in the hardware. It is also essential that fundamental "cause-effect" relationships be developed so that appropriate control strategies can be applied. This requires a better fundamental understanding of the operation of the treatment plant process.

The industry has demonstrated that, on process units under severe conditions, real-time control is viable. Although automation has been applied in treatment facilities, real-time control to any large extent is non-existent. However, process optimization through real-time control may represent the most cost-effective option to meet the toxics and toxicity control requirements of the 1990's.

Summary

There were several recurring conclusions and recommendations for further developmental work which were brought forth at more than one of the workshops. These represent the key findings of the workshop sessions and include the following:

- Although existing activated sludge-based wastewater treatment systems, that are properly designed and operated, are capable of providing a high level of toxics and toxicity control, source control and effective pretreatment are essential to efficient biological system operation. Innovative source control programs are needed. On-line instrumentation development should focus on influent wastewater quality monitoring as well as monitoring of process operating condition.

- SPC procedures have been demonstrated to be effective in reducing the variability of treatment plant performance as well as monitoring and improving the effectiveness of source control programs.

- There is a need for the development of an industry-wide, standardized data management approach which would eliminate the inconsistencies apparent at present. This data management system must provide for detailed data analysis as well as data logging for regulatory purposes.

- A thorough review of the variability of chemical analysis (trace and conventional contaminants) data and biomonitoring data is in order. Regulatory agencies are more frequently placing numerical limits on effluent quality at near detection limit levels without due consideration for the analytical variability associated with these numerical values.

- Standardization of biomonitoring procedures and QA/QC protocols is needed to provide the industry with some degree of confidence in these test results.

- Implementation of real-time process control strategies based on on-line monitoring instrumentation hinges on the demonstration of the long-term effectiveness of automatic process control. A phased approach is recommended which would involve initial demonstration of the practicality of on-line measurement of key performance indicators followed by a phase-in of closed-loop control after the instrumentation is proven and 'cause-effect' relationships are established.

Key words: Petroleum Refinery Wastewater Treatment, Toxic Contaminants, Toxicity, Process Optimization, Instrumentation and Control.

References

Cheremisinoff, N.P. (1988), "Computer statistics for environmental engineers". *Pollution Engineering* January, 54–62.

Gabaldon, D. (1988), "Database Management via 1-2-3". *Byte* May, 171–176.

Laffly, G. (1989). Personnel communication.

PC Magazine (1989), "Attractive Alternatives: Lotus 1-2-3 Add-Ons". March, 230–231.

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